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BINDER MATERIALS FOR MODIFICATION OF FUNCTIONAL NANOPARTICLE COATING

Master of Science Thesis

Examiner: prof. Jyrki Mäkelä
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ABSTRACT

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There are lots of changes happening in the field of surface modification. The purposes of this thesis is to present a surface modification procedure that could be useful in producing durable coatings from nanoparticles. Generally, there are three ways to modify a surface: change the structure of the material, remove material or add material. Liquid Flam Spray and spin coating processes for adding material to the surface were explained in this research.

Since the mid-twentieth century, the interest for usage of natural materials has declined. We want to change this trend and from four binders that were used in this thesis, three of them are natural (pine tar, Zein and gum arabic) and just one of them is a polymer (PMMA). Three different coatings were made from all of the materials in different concentrations (0.2, 1 and 5%). Pine tar and PMMA were dissolved in acetone, gum arabic in water and Zein in ethanol 70%.

The prepared solutions were spin coated on top of the clean glass substrate for producing thin film from each concentration. All samples were heat-treated in an oven in order to solidify the thin layer of film on the substrate. Titanium dioxide nanoparticles were deposited on top of the binders by Liquid Flame Spray (LFS) technique. Photocatalytic activity of the samples after scrubbing and ultrasonic bath were tested in order to understand which binder performs best in fixing the nanoparticles on top of the substrate. The results were shown in the graphs, where the concentration of methylene blue changes as function of UV exposure and activity of TiO_2. SEM images of the binder coatings were prepared to see the surface structure before and after the nanoparticle deposition.

Result evaluation revealed that the pine tar with 1% concentration is better than the other binders in any concentrations tested and, also, Zein was shown to have acceptable results compared to gum arabic and polymethyl methacrylate (PMMA).

PREFACE

This research is my master thesis for the conclusion of my master degree at the faculty of Natural Science in the Tampere University of Technology (TUT). Durability of surfaces that include a thin coating of nanoparticles is a still challenging even today. Also, finding binders and adhesives which are nature friendly is also challenging. The idea of this research came from combining these two matters and finding the solution for stabilizing nanoparticles on top of a substrate. The project was fascinating because there were natural materials, which have never been tested before as adhesives or binders for nanoparticle coated surfaces. The results answered the questions that we identified beforehand.

At first, I would like to thank my supervisor Prof. Jyrki Mäkelä, the head of the laboratory. He gave me a lot of information, opportunities and the facilities to fulfill this project. Without him, I could not have had such a great experience in the aerosol physics lab. He always accepted my new ideas and supported me to test and work on them.

I also want to appreciate my colleagues, Markus Nikka, who helped me in the process of liquid flame spray coating, Paxton Juuti for guidance in thesis writing process and Mari Honkanen for preparing the SEM images. In addition, I would like to appreciate the Academy of Finland for supporting this project and giving me the chance to prepare materials and devices that were needed in this research. Last but not least, I extend my gratitude to my husband for the kind words and keeping me motivated in difficult and challenging situations in all processes of doing my research.

Tampere, 22.5.2018

Elham Baniadam

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LIST OF SYMBOLS AND ABBREVIATIONS

CB	Conduction Band
CVD	Chemical Vapor Deposition
GA	Gum Arabic
IBAD	Ion Beam Assisted Deposition
LFS	Liquid Flame Spray
MB	Methylene Blue
MEMS	Micro-electrochemical system
PH	Potential of Hydrogen
PVD	Physical Vapor Deposition
SEM	Scanning Electron Microscope
UV	Ultra Violet (light)
VB	Valence Band
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
K	Potassium
Mn	Manganese
Na	Sodium
Ni	Nickel
P	Phosphorus
Zn	Zinc
OH	Hydroxyl
PMMA	Polymethyl methacrylate
TiO_2	Titanium dioxide
TTIP	Titanium (IV) isopropoxide
C_0	Concentration of methylene blue solution before UV exposure
C	Concentration of methylene blue solution after UV exposure
t	Time
k	Reaction coefficient

1. INTRODUCTION

Numerous regular and advanced mechanical applications require materials with well-characterized surface properties, satisfying specific needs, which go for both valorizing the material and advancing the related technology. For this reason, surface functionalization of materials has turned out to be a standout amongst the most dynamic research regions lately. The meaning of surface functionalization has a few variations, however it can simply be viewed as a route to introduce new properties to a specific material, planned to satisfy particular prerequisites.

Surface functionalization has been known for a long time and has been utilized for many years. These days, the advances in surface designing, nanotechnology and nanomaterials permit the control of the composition of materials down to the sub-atomic scale, paving way for new high tech practical materials. Surfaces of numerous materials can be functionalized by applying coatings. The origin of practical coatings is implanted in the legacy of humankind and known cases are, e.g., the protection of the primary metallic devices and antiquities (brass, iron and silver) with gelatins, animal fats, beeswax, vegetable oils and different minerals. The idea of a useful covering has been in a long development and today numerous ways for surface functionalization are accessible. Still, some of those antiquated surface modifiers are still utilized today due to their remarkable properties.

Coatings, regardless of whether they are organic, inorganic or hybrid, are a class of materials that can be custom fitted for most applications in which they need to have the capacity to perform a specific function. There are various ways of doing coatings for different applications that are part of our everyday life. Coating technologies are used in the manufacturing of cars, home furniture, solar cells, or further developed applications, for example, therapeutic gadgets and orthopedic implants, radars or satellites. In recent years, research in nanotechnology and nanomaterials has developed many new useful coatings and this pattern will keep developing in the following years. Practical and smart coatings are without a doubt a class of materials with a tremendous innovative interest (Montemor, 2014).

Sometimes in order to have a better coating, adhesive materials play an important role. Simple definition for adhesive is any substance that is fit for holding materials together in a useful way by surface connection that opposes separation. Natural adhesives come essentially from vegetable or animal source. Despite the fact that the interest for natural products has declined since the mid-twentieth century, some of them keep on being utilized, like wood and paper items, e.g. layered board, bottle marks, envelopes, bookbind-

ings, containers, furniture, and so on. In addition, because of different environmental regulations, natural adhesives obtained from renewable resources are also getting more attention (Pike, 2015).

In this research both natural and synthetic adhesives namely pine tar, Zein and gum arabic and PMMA were used. Starch is removed from wheat, corn, rice, or potatoes. They form the principle kind of vegetable glues that are dispersible or soluble in water and are gotten from plant sources all through the world. Dextrin and starch glues are utilized in wallpaper glue and packaging as well as corrugated board. Gum arabic is obtained from acacia trees by making artificial wound in tree to cause the gum to discharge.

Polymers utilized in synthetic adhesives divide into two general groups, thermosets and thermoplastics. At normal temperatures, thermoplastics produce strong, durable adhesion, and for some applications, they can be softened just by heating without any degradation. PMMA that is used in this research belong to thermoplastic resins (Pike, 2015).

2. THEORETICAL BACKGROUND

2.1 What is Nanotechnology?

Nanotechnology works on small-sized structures or materials. One nanometer is defined as 10^{-9}m (one billionth of a meter) which means that nanotechnology deals with materials at the atomic or molecular level. Research shows that materials in micro scale exhibit physical properties the same as bulk form but in nanometer scale may show different physical properties than bulk form. For example, small silver particles show antimicrobial feature that is not obtained from larger silver particles (Matsuura, 2006, p. 10), also bulk semiconductors change to insulator when the characteristic dimension is in couple of nanometers (Cao, 2014, pp. 1-3).

The above examples show why nanotechnology has become so popular nowadays, because just by changing the size of materials to nano-scale we will have changed physical or chemical properties. Nanotechnology can also be used for pharmaceutical purposes, as an example carbon nanotube can deliver a drug in the bloodstream or in micro-electro-mechanical system (MEMS) and so on.

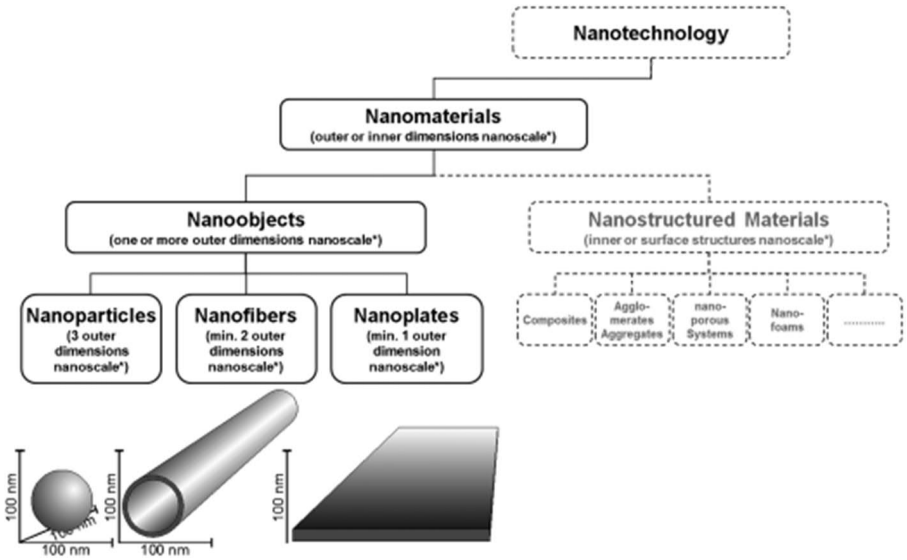


Figure 1. *Nanoobjects include nanoparticles, nanofibers and nanolayers or nanoplates* (Krug & Wick, 2011)

Nanostructured materials such as nanoparticles, nanowires, thin films, nanorods which have structures in nano-scale should have at least one dimension less than hundred nanometers (Figure 1). Fabrication of nanomaterials and nanostructures demands different technology (Cao, 2014, pp. 1-3).

There are several ways to classify nanostructured materials. The two most important systems used are based on characteristic of the materials and on the dimension of the material. By considering the dimension, there are three groups for nanostructured materials. The first group has only one dimension in nanometer. Nanofilms are the best examples of this group. The second group has a common tubular fiber structure with two nano dimensions. Carbon nanotubes, nanowires and nanofilters are examples of this group. The third group has three dimensions in nanometer. Nanoparticles, nanocapsules, nanopowders and quantum dots are examples of this group. Different groups are obtained by characteristics of material-based system: lysosome and biological nanoparticle (e.g. proteins and peptides), carbon based nanomaterial (e.g. functionalized fullerene), organic/inorganic hybrids (i.e. nanocomposites), inorganic nanoparticles (e.g. silver, gold, iron or iron oxide nanoparticles) and organic nanoparticle (e.g. dendrimer, polymer).

Nanoencapsulation, nanodevicing and nanocoating are three main important modification techniques. In nanoencapsulation, combination of two or more baseline input materials is used for synthesis of a new material. For active gradient transportation system which is movement of molecules and ions across the cell membrane from a lower concentration area to higher concentration area against the concentration gradient (Demirel, 2014) and medicine's development nanoencapsulation is a useful technique. Generally, anticancer medicines are produced by this technique. Combination of nanomaterial science, nanoelectronic and biotechnology knowledge is needed for nanodevicing. Nanodevicing is the result of nanostructured material's modification into a nanodevice. The production of solar cells, electrical transducer polymers and thin film sensors from nanofilms are examples of nanodevicing. Nanocoating is an ordinarily utilized nanomodification method. It is similar to nanoencapsulation but not the same. Nanocoating does not develop a shelled material or spherical shape material necessary (Wiwanitkit, 2008, pp. 21-23).

Since nanotechnology is a relatively new area in science, we just focus on its usefulness but it is necessary to check side effects and problems as well. In history, there are numerous examples of side effects of new things that have shown to be unpredictable in the long-term usage, for example, the congenital defect because of the utilization of thalidomide. Prevention of a similar situation need to be discussed regarding nanoproducts. It is necessary to have nanotoxicology study (Wiwanitkit, 2008, p. 173).

Many nanomaterials, which are fabricated in industry, have gone through relative risk assessment. Quantities of the inventoried materials and physical-chemical features of materials can be used in order to have relative risk assessment based on items such as toxicity, flammability, volatility, persistence and carcinogenicity. At the present time safety of nanotechnology is the one main goal of nanoscience (Wiwanitkit, 2008, pp. 21-23).

2.2 Surface coating methods

One of the science and technology fields is tribology that tackle with interacting surfaces in relative motion, which means it works with situations connected to wear and friction. In industry, it is necessary to control or reduce the wear or friction for many cases, such as to increase the lifetime of bio-system and machinery, to manufacture devices and engines more effectively. Two main factors have supported the development of surface engineering. First one is the improvement of new treatment strategies and coatings that produce tribochemical properties and coating characteristics, which were not achievable before. The second factor behind the development of this branch of knowledge has been the identification by material researchers and engineers that the surface is the most essential part in numerous engineering elements. Many failures rise at the surface, either by corrosion, fatigue or wear (Holmberg & Matthews, 1994, pp. 1-6).

Today, tools and mechanical components confront more performance demands. Surface coatings generate the chance for material design in which the particular properties are located where they are generally needed. Toughness and strength can be designed for the substrate materials when the coating is in charge of the resistance to wear, corrosion and thermal loads (Wiwanitkit, 2008, pp. 1-6). The entire coated surface structure with its functional parameters and properties can be seen as a composite framework to be enhanced to obtain greatest benefit. This, generally, indicates the major reasoning of surface engineering that has been explained by Melford in 1991 as the design of substrate and surface together, as a structure to provide a cost effective performance. The surface building strategies incorporated into this general order appear in figure 2.

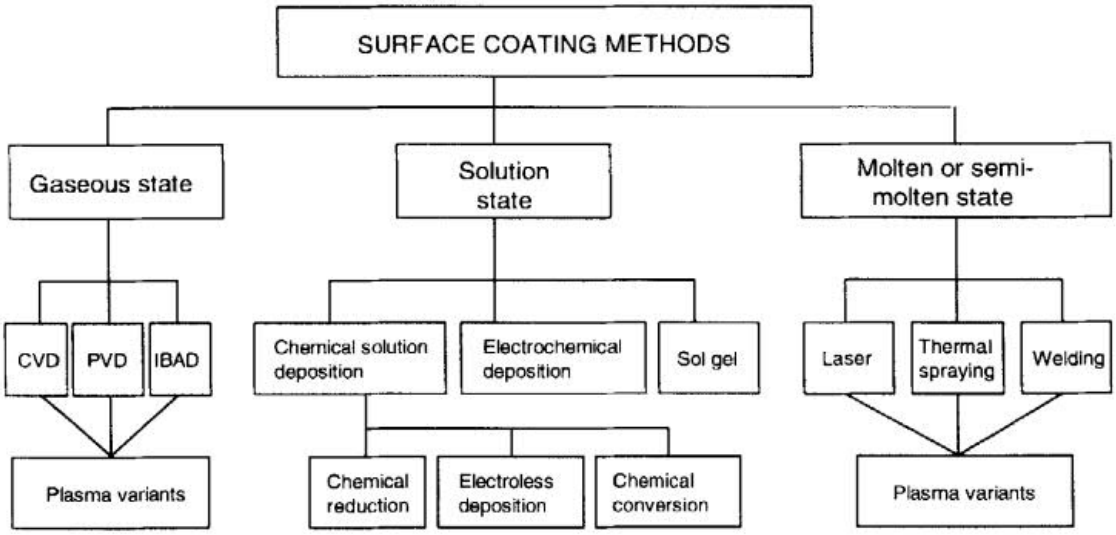


Figure 2. *Common categorization of surface engineering* (Holmberg & Matthews, 1994, pp. 7-32)

Table 1. *Comparison between main coating methods (Holmberg & Matthews, 1994)*

	Gaseous state processes			**Solution processes**		**Molten or semi-molten state processes**		
	PVD	**CVD**	**Ion implantation**	**Sol-Gel**	**Electroplating**	**Laser**	**Thermal spraying**	**Welding**
Deposition rate (kg/h)	Up to 0.5 per source	Up to 1		0.1 - 0.5	0.1 - 0.5	0.1 - 1	0.1 - 10	3.0 - 50
Component size	Limited by chamber size			Limited by solution bath		May be limited by chamber size		
Substrate material	Wide choice	Limited by deposition temperature	Some restrictions	Wide choice	Some restrictions	Wide choice	Wide choice	Mostly steels
Pre-treatment	Mechanical/chemical plus ion bombardment	Mechanical/chemical	Chemical plus ion bombardment	Grit blast and/or chemical clean	Chemical cleaning and etching	Mechanical and chemical cleaning		
Post treatment	None	Substrate stress relief/mechanical properties	None	High temperature calcine	None/thermal treatment	None/substrate stress relief		None
Control of deposit thickness	Good	Fair/good	Good	Fair/good	Fair/good	Fair/good	Manual variable automated good	Poor
Uniformity of coating	Good	Very good	Line of sight	Fair/good	Fair/good	Fair	Variable	Variable
Bonding mechanism	Atomic	Atomic	Integral	Surface forces		Mechanical/chemical		Metallurgical
Distortion of substrate	Low	Can be high	Low	Low	Low	Low/moderate	Low/moderate	Can be high

Table 1 sums up strong and weak points of most important coating processes in industry. It shows three main processes such as gaseous state processes, solution state processes and molten or semi-molten state processes and all those three processes include some sub-group methods. Following part will discuss about definition of each sub-group individually.

Physical Vapor Deposition (PVD) is a type of vapor deposition where the substance is evaporated and again condensed to coat the substrate. The fundamental thought behind PVD is the physical state of the material changes and gets deposited to the targeted material. There are two principal ideas that are utilized to vaporize the material. First, the material can be evaporated via thermal heating or melt the surface of the material with laser or electron beam. Second, the material atoms can be removed from the target surface by transferal of momentum from incident particles, such as ions. This kind of material removal is called sputtering. Single element or a compound can be used for coating. Compound can be delivered by blending the evaporated element with another element mostly in the gas phase (Vadiraj & Kamaraj, 2010, p. 16).

Chemical Vapor Deposition or CVD method is a very strong technique for the synthesis of porous or dense nanostructured films. In the CVD method, a minimum temperature for the substrate is 300°C to completely oxidate or react the precursors (Tricoli, et al., 2010). In this method, gases including volatile mixtures of components or components to be deposited are inserted into the reaction chamber then after reactions they condense on the substrate to make a coating. In CVD deposition, pressure can be set from 1 Pa or less to atmospheric. Additionally, there are different methods for helping the procedure, for example, using electron beam or laser, or by ion bombardment of the developing films (Holmberg & Matthews, 1994, pp. 7-32).

In ion implantation method, surface of material is bombarded with specific ions that have energy around 100 keV. On metallic substrate, ions penetrate into the material and they are fixed there. Ions lose their energies after impacting with the atoms of the substrate. Some benefits of ion implantation are, surface hardness increasal, there is no geometric deformation in final product and it can be used for polymer, metal and elastomers (Holmberg & Matthews, 1994, pp. 7-32).

The sol-gel process is a wet chemical method for the synthesis of a variety of nanostructures, in particular metal oxide nanoparticles. In this way, the molecular precursor (usually metal alkoxide) is dissolved in liquid converted to the gel by hydrolysis/alkalization by heat and stirring. Later the gel needs to be dried. After drying the gel, it was powderd and heated until the materials thermally decomposed. The sol-gel method is inexpensive and due to being a low temperature technology, it can be controlled properly based on the chemical composition of the products. Sol-gel can be used in the ceramic manufacturing process as casting materials or as an interface between thin films of metal oxide for various processes (Holmberg & Matthews, 1994, pp. 7-32).

In Electroplating method, the galvanic treatment of a metal is based on electrochemical reactions. It is necessary to use an external source of current to make the reactions go in the desired direction. Specific reactions in the anode and cathode are always present in electrolyte simultaneously. The electrolyte solution should contain metal ions and, since the ions of metal have a positive charge, they tend to move in the direction of the electrodes or polar electrodes (negative pole or cathode) due to the absorption of the opposite loads. The opposite pole, which has an electron deficiency, is called the positive pole or anode. In general, the typical coating cycle can be considered as follows: an atom in the anode loses one or more electrons and becomes a positive ion in the coating solution. The positive ion is attracted to the cathode, the place where electrons are accumulated and moved in it. This ion takes the lost electrons in the cathode and after depositing it into the atom, it is partially deposited from the metal (Schlesinger & Paunovic, 2011).

Laser coating, laser spraying or laser cladding is an advanced coating method to improve properties of the surface of different equipment and components. This coating has non-porous, crack free and very dense microstructure. In addition, laser coating demonstrates great metallurgical bonding to the base material, has uniform coating thickness and composition. Laser coating makes extremely low dilution and low heating input to the element. Surface of the new component has good resistance in front of the high temperature, corrosion and wear. This method can also be used to repair worn components. Laser coating is a deposition procedure, where wire or powder as the coating material is applied to the surface of the base material via a melting procedure. Powder takes energy from the laser beam and starts warming, melting and deposits to the material surface. In this process surface also absorbs part of the heat that cause controlled melting of very thin surface of the base material. This makes metallurgical bonding between the base material and the coating (Vuoristo, et al., 2005).

The raw materials used in thermal spraying are typically in powder, wire or rod form. The materials are melted or molded by a source of energy, and in the next step, the particles of the materials are surrounded by neutral gas and accelerated to the prepared surface of the unit. Due to the high acceleration, when a particle hits the surface of the substrate, there is a strong mechanical bond between the particles and the surface. The particles, due to collisions with the surface of the piece, are deformed and form a layer structure. Recently, liquid sources of materials have been used in thermal spray jet. The liquid can be a solution of various precursors such as a mixture of nitrate in ethanol/water, metal organics in isopropanol, mixture of nitrates, etc. At the end, nanostructured coating is made with thickness of about 5-100 μm (Fauchais, et al., 2014). The use of thermal spray technology has several advantages over other coating methods. One of the main advantages of the process of thermal spraying, in comparison with other surface coating method, is the possibility of creating a wide range of different coatings on the substrate of the desired component. In fact, all materials that can be melted without decomposition

can be used to create a coating by thermal spraying. The other advantage of thermal spraying is that during the spray application process. The surface does not actually heat up much, so there is no destructive heat affects due to the component's warming. One of the limitation of this process is that there can be points of coverable surface that cannot be seen by the torch tip; however, this limitation has greatly been addressed by improving the shape and design of the new thermal spray equipment, as well as the use of advanced robotic systems.

The thin film coating method used in this thesis is Liquid Flame Spray. It is a development from thermal spray technique where liquid is used as a precursor. This method is presented in more detail in chapter 3.2.

Different welding techniques can be used to deposit the vast range of metal/ceramic and metal composites. Arc welding and oxyacetylene are the two most used techniques. These two methods can be utilized for many metals. However, these methods for coating of non-ferrous materials that having melting points beneath 1100°C mostly are not recommended. Generally, the thickness range is between 1.5 to 6.0 mm. Materials for coating are typically applied to resist abrasive wear and generally have chromium carbides, boron distributed in combination with iron or tungsten, nickel or cobalt. Processing path can influence the coating properties by selecting different materials (Holmberg & Matthews, 1994, pp. 7-32).

2.3 Coating characteristics

In engineering coatings, there are tens of important properties such as thickness, adhesion, surface finish, corrosion, resistance, friction/wear performance, hardness, porosity, composition, internal stress, structure and morphology. The surfaces of bulk materials like the surface of coatings have certain characteristics that may vary from the materials within coating. For instance, there will be generally an oxide film at the surface of the chromium coating. Likewise as with a bulk material, when a coating exposed to the final mechanical treatment like polishing, may present the influence of near surface distortion. It is good to know these localised differences in the nature of the coatings, particularly where the quick contact with the counterface happens. Absorption, chemisorption and wettability effects can be controlled by interface across the coating and its counterface.

Topography and geometrical properties of surfaces are important. Substrate gets new significance after coating, and deposition technique sometimes can affect the surface topography. Some coating technique like electroplating especially can smoothen the substrate surfaces. Some thermal spraying methods can roughen surfaces.

Thickness can be represented by concepts like mass thickness that seeks to identify that film have different porosities and densities. Without quantification of porosity or density, the height measurement would be meaningless in many applications.

It is important for the coating to stay attached to the substrate under the operating situation. The minimum adhesion is needed for a coating to stick to the substrate is the simple definition for coating adhesion. Good coating adhesion depends on structure of atomic bonding, state of stress and elastic moduli, fracture toughness, purity and thickness. Therefore, interactions between the substrate and coating affect the coating adhesion (Holmberg & Matthews, 1994) .

There are many available techniques that produce chemical composition or other information about coatings. Different materials or chemicals or even mixture of different chemicals can be used to formulate the coating. Each component in the formulation represents a specific feature. There are four common components such as additives, binders, pigments and carrier fluids. Additives are varies and can be used as flow agents, stabilizers or curing agents. Binders are resins or polymers. Binders are adhesives between surface and solids. Pigments are insoluble solids and they can be used for aesthetic quality. Carrier fluid is generally a liquid like water or an organic solvent. Coatings can be made from grains or polycrystalline, either arbitrary or texture with favored orientation like sometimes can be epitaxial or amorphous (Holmberg & Matthews, 1994).

3. METHODS AND MATERIALS

3.1 Spin coating

Spin coater is used to coat a surface of the substrate by rotating method in order to have a thin film. At first, substrate is placed on top of the chuck (rotational surface) and will attach on it by applying vacuum. Then liquid is added on top of the substrate (glass, metal…) or sprinkled on the center of the substrate surface. In the next step rotational speed is set to desired speed which can be from 1000 to 12000 rpm (round per minute) in order to spread the fluid. Eventually thin layer of coating is formed on top of the substrate (Figure 3(a)). Solvent evaporates and only layer of coating will remain when the liquid contains evaporating solvent. This method is based on centrifugal force, which causes the fluid to cover the whole substrate (Aliofkhazraei, 2015).

In this method, factors such as solvent adhesion, rotational speed, time of the rotation and acceleration play important role. For example, for making thin layers of coatings rotational speed should be high and rotating time must be long and vice versa for thick coating.

Spin coater from Chemat Company was used in this research (Figure 3(b)). It has two stages of timer and speed control and rotating speed is tunable from 500 up to 8000 rpm.

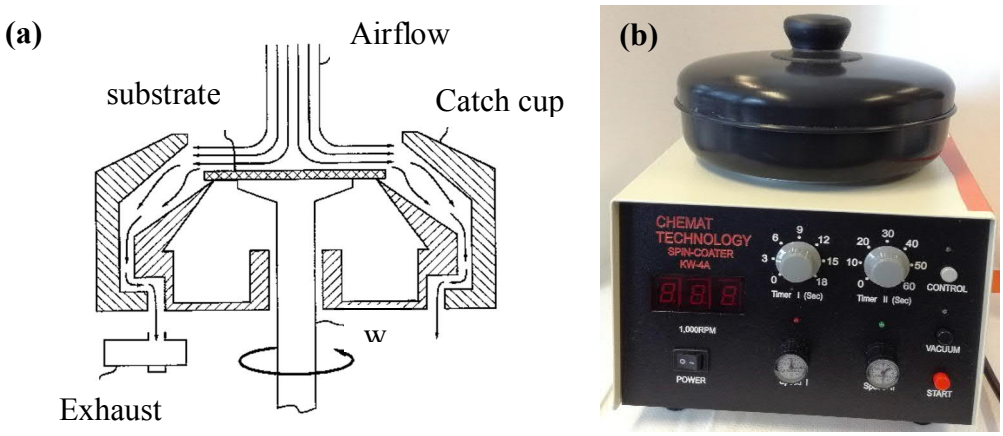


Figure 3. *a) Schematic diagram of Spin coating* (Larson & Rehg, 1997)*, b) Spin coater from Chemat Company*

Spin coating has been used to make thin films and wildly used to produce magnetic disks, optical mirrors, devices for solar cell, sensors, detectors, DVD's and CDROM's, anti-reflection coatings and integrated circuits etc. (Sahu, et al., 2009)

3.2 Liquid Flame Spray (LFS)

Liquid flame spray (LFS) is a technique to produce and deposit nanoparticles. This method is used to coat different substrates such as glass, metal or paperboard. Different surface properties can be designed like adhesion, wettability or electrical properties by using LFS (Teisala, et al., 2010).

In this method, metal or metal oxide solutions are fed to the spray gun with oxygen and hydrogen in different ratios. Micron-sized droplets are formed when precursor exits the nozzle. The droplets are vaporized and they move further from the nozzle and nucleation, coagulation, sintering and agglomeration processes take place at different parts of the flame (Figure 4). In the final stage, formed nanoparticles are attached to the substrate (Teisala, et al., 2010).

The main operating principle of Liquid Flame Spray is high temperature, turbulent (Pitkänen, et al., 2005) and hydrogen-oxygen high velocity (Keskinen, et al., 2008). Combustion gases (hydrogen, oxygen and some case nitrogen) are directed into the flame, also precursor solution is injected, via thin needle that is located in the middle of burner, into the flame. Hydrogen is used for atomizing precursor's liquid. In the burner nozzle the speed of the hydrogen flow can be around the speed of sound. The main fuel source in the combustion is the hydrogen flow. Organic solvent or alcohols can be in the precursor liquids that play a role of a fuel in the flame, but water-based precursor liquids can also be used (Tikkanen, et al., 1997) and (Pitkänen,2005).

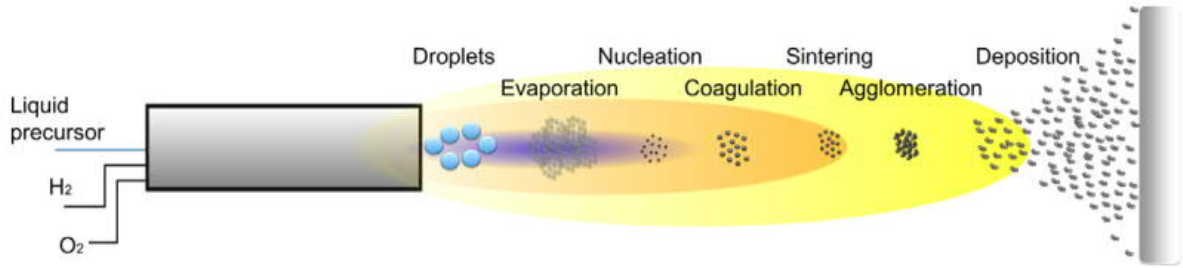
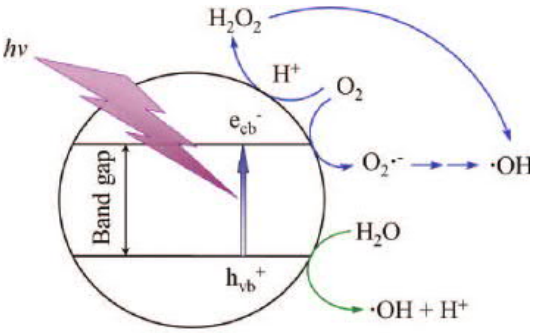


Figure 4. *Schematic diagram of Liquid Flame Spray (LFS) process and nanoparticle deposition on top of the substrate* (Haapanen, et al., 2015)

Size of the particles can be controlled by tuning the precursor concentration, flow rates and the distance between the burner and a substrate. In LFS method, the primary particle size for generated nanoparticles can be set from 2 nm up to 50-100 nm (Aromaa, et al., 2007). In this technique, the flame temperature varies from 600 up to 2500°C. Flame size and temperature is tuned by controlling the combustion gas feed rates and the precursor (Aromaa, 2012).

3.3 Testing of photocatalysis

Photocatalyst can be used as an environmental cleaner when exposed to sunlight or fluorescence. It eliminates contaminations and organic compounds. Generally, photocatalysis is a process that absorbs energy of light equal or larger than the band gap of a semiconductor material; electron is excited from valence band (VB) to the conduction band (CB). This charge separation leads to the generation of electron-hole pairs that can produce free radicals in the system for redox of substrate (Figure 5(a)). Free radicals such as OH are great oxidizers of organic materials that degrade pollutants (Soltani, et al., 2012).



(a)

(b)

Figure 5. (a) *Schematic diagram of photocatalytic process* (Wang & Xu, 2012)*, (b) Camera set up for photocatalytic test*

Generally, photocatalytic activity is determined with spectroscopic techniques, like Raman or absorption spectroscopy (Houas, et al., 2001). However, a standardized technique has not been established and no specific instrument is needed to precisely show photocatalytic activity as a function of time. The used method is based on photocatalytic degradation of methylene blue (MB), $C_{16}H_{18}CN_3S$, and its ability to change from blue to transparent as a function of its concentration. The method can be classified with the following steps.

1. Sample with TiO_2 coating is put in the MB solution.
2. Color value (D) of the solution is photographed (equation 1)

$$D = \sqrt{(R_2 - R_1) + (G_2 - G_1) + (B_2 - B_1)} \quad (1)$$

3. Methylene blue solution and sample are exposure by UV light
4. Steps 2 and 3 can be repeated for as many times as is needed
5. Methylene blue concentration (C) and reaction rate (k) can be obtained from the following equations (2) and (3)

$$-\ln \frac{C}{C_0} = kt \quad (2)$$

$$C = 1 - D = C_0 \, e^{-kt} \quad (3)$$

In above equations, C_0 is the concentration of methylene blue solution in the beginning of the measurement and C is the concentration of methylene blue solution after time t of UV exposure. Slope of the linear fit to ln (C_0/C) was used to evaluate reaction coefficient k. Unit of reaction coefficient k is 1/s (Juuti, et al., 2017).

Methylene blue can be used as an accessible dye to estimate the photocatalytic activity of nanoporous surfaces. This technique requires minimum amount of equipment, but creates outstanding results. This method can be used for evaluating concentration value and rate constant as a function of time.

In appropriate ranges, the concentration of methylene blue solution can be directly related to the color intensity of the image that is taken. In order to set the measurement range, this system must be calibrated to the reference solution with a known concentration. The sample is then compared against both of the primary methylene blue solution and a completely degraded solution. Reaction rates and the concentration of the methylene blue solution can be calculated after several rounds of color value logging and UV-light exposure (Figure 6).

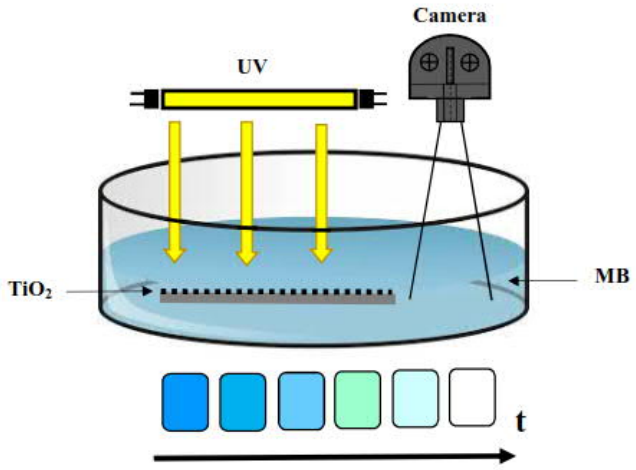


Figure 6. *Demonstration of the sample's UV exposure and photo taking. Changing of the color of the methylene blue solution is also illustrated as a function of the exposure time.*

In this work, the photocatalytic degradation of the methylene blue was studied by using titanium dioxide nanoparticle catalyst under UV exposure. Methylene Blue solution (0.015 mMol) was made by diluting the initial powder with deionized water. A 30 ml of solution was used for each sample and the samples were put in UV chamber, which contains UVB-laps (six Sankyo Denki 15 W UVB). The UV exposure times between imaging were chosen to be 0, 10, 20, 40, 70, 100, 130 and 150 minutes. A camera, Canon 7D Mark II with 50 mm objective, was used to take a picture after each exposure time. Exposure time and aperture were adjusted to 1/80 s and F1.8 respectively. Also, the lens distance from the sample was kept at 27.5 cm (Figure 5(b)).

Part of the image that is not obstructed by the sample, creates a color value as a function of the irradiation time that is plotted as (1 – D) to show the decay of the concentration.

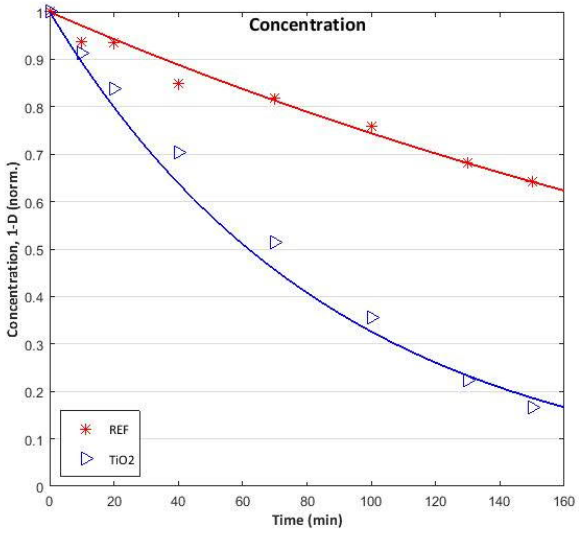


Figure 7. *Concentration of the MB as a function of time.*

Figure 7 illustrates the exponential decay of the methylene blue as a function of time for a sample with a titanium dioxide nanoparticle coating and its reference (a clean glass without coating). Concentration C at time t with the primary concentration C_0 can be normalized to obtain the pseudo first order rate constant k with a linear fitting.

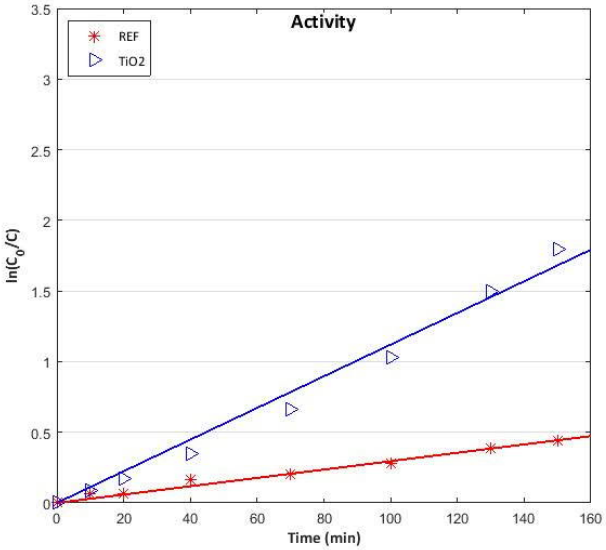


Figure 8. *Linear behavior of MB degradation as a function of time for the TiO_2 nano-particle coated sample and the clean glass as reference*

Fitting for the rate constants is demonstrated in Figure 8 for a titania coated sample and its reference. Reaction rates were calculated to be 0.0112 1/min and 0.0030 1/min, respectively.

3.4 Binders

Pine tar (Terva in Finland) is obtained from pine-wood, and has probably been produced in Scandinavia since the Iron Age. For hundreds of years, it was the most important export good of Sweden to protect wood, including deck and rig of ship, while exposed to harsh conditions Still nowadays, pine tar is used for treating wooden furniture and flavoring food, candies and alcohol and on the baseball bat's handles to improve grip.

Also in ancient Greece, pine tar was used. In fact, Hippocrates first described the use of pine tar in medicine more than 2000 years ago. Today pine tar, which is still made in a traditional way in Turkey's villages, is still used for medical purposes. Over one hundred years ago, pine tar products have been manufactured and used for skin disease treatment like eczema and psoriasis, also it has uses in shampoos, tooth-powder, disinfectants and deodorants.

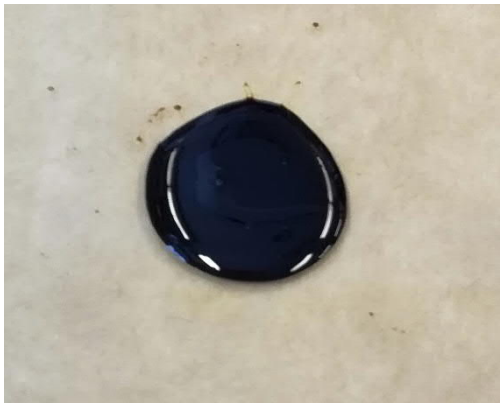


Figure 9. *Pine tar has dark brown or nearly black color.*

Pine tar is a dark brown or nearly black liquid (Figure 9) that has a higher viscosity than water and has sharp taste and odor. Pine tar is soluble in alcohol, ether, acetone, chloroform and glacial acetic acid but only slightly soluble in water. Pine tar components varies due to the pyrolytic process parameters of manufacturing, for example; method, temperature and duration. Also the parameters of the wood, like the age of the trees, moisture condition when tree was growing and the soil type affect the quality of the pine tar (Barnes & Greive, 2017).

Zein is one of the main corn storage proteins, which contains 45-50% of the proteins of the maize. Despite its low nutritional value, it has a specials place in the synthesis of

biopolymers and biodegradable film, due to its unique ability to form anti-oil, waterproof, transparent and impermeable coatings to microorganisms. Zein has a good potential for some applications. Numerous efforts have been made to provide a commercial and low cost process for producing Zein. Research continues to improve the condition for extraction, production, purification and treatment method for Zein.

Zein can dissolve in aqueous alcohol but has a poor solubility in water. This behavior of solubility can be explained with a high proportion of nonpolar amino acid residues and deficiency in basic and acid amino acids. Zein is classified into four groups of α, β, γ and δ according to its solubility properties. Glossy, tough, hydrophobic and greaseproof coating are made out of Zein which are resistant to microbial attack. Coating with and making thin films out of Zein are its most promising applications, especially in the drug and packaging industry respectively. Additionally, cross-linking agents such as formaldehyde, butanetetracarboxylic and citric acid can make plasticized Zein film that has two to three times more tensile strength (Shukla & Cheryan, 2001).

Two important features of Zein, nontoxicity and biodegradability, make it a good natural polymer for use as a scaffold in wound healing, in food packaging and in drug delivery systems. Zein has typically been blended with other biopolymers such as collagen, silk, chitosan, poly (L-lactide) and polycaprolactone.

Figure 10. (a) *Zein is obtained from corn kernel and has a powder form in yellow color, (b) Molecular structure of Zein* (Ali, et al., 2014).

Figure 10(b) shows the molecular structure of Zein (Ali, et al., 2014). Zein that was used in this research purchased from Sigma-Aldrich, which is the yellow powder. Figure 10(a) shows the appearance of Zein.

Polymethyl methacrylate (Acrylic, PMMA) is one of the most widely used engineering plastics in the polymer industry (Figure 11(a)). The main cause of its high demand is due to its high clarity. PMMA exhibits excellent optical and water resistant properties, and is extremely resistant when exposed to atmospheric conditions (temperature, pressure and

moisture) (Lyoo, et al., 2004). Density of PMMA is 1.19 g/cm^3 and the melting point, the boiling point and the glass transition temperatures are 180°C, 200.0°C and 114°C respectively (Thejo Kalyani & Swart, 2017, p. 262). Methyl methacrylate is the PMMA monomer, which is extremely irritating to the skin, eyes and respiratory system. Methyl methacrylate also has a sharp odor. Carbon dioxide and carbon monoxide are the two main thermal decomposition products of PMMA (Kosa, 2017, p. 73)

This material has the ability to be cut, formed, smeared, punctured, bent and so on. This material is one of the components of optical fibers. PMMA has excellent optical clarity. Conventional PMMA transmits up to 92% of light, which is more than other materials, including glasses and plastics. Because it is resistant to UV rays, it is also used for equipment that is exposed to outdoor environments. In fact, this material can be used for a long time in such spaces without changing the color (Pawar, 2016).

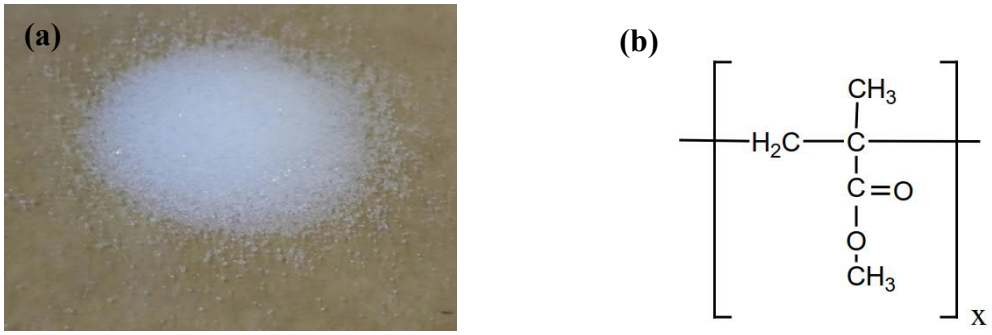


Figure 11. (a) *PMMA granules with particle size of 600 microns, (b) Molecular structure of PMMA, X indicates a repetition of its building units* (Van De Walle, 2015)

The surface of PMMA is very resistant to scratches and damage. This feature is very practical and useful in cases where visual clarity is important to the use in the long run. It has the ability to be improved by combining with other materials that enhance its properties for special applications. PMMA demonstrates a wide range of usage and is a suitable replacement for glass in aircrafts and cars (dashboard, light cluster, porthole, canopies), in furnishing (shop signs, anti-noise walls, display units) and in medical usage like contact lenses, teeth and bone cement (Duval & Lebrun, 2006).

Gum Arabic (GA) or gum acacia is a natural polysaccharide obtained from Acacia Senegal tree (Figure 12(a)). It has great properties like solubility, nontoxicity, PH stability and antioxidant activity. Gum arabic has numerous applications in cosmetic, pharmaceutical industry, textile, food industry, lithography and pottery (Thomas, et al., 2013, pp. 217-808). Molecular structure of GA consists of 1-3 linked β-D galactopyranosyl units and carbohydrates like glucuronic acid, arabinose and rhamnose (Johnson & Berkel, 2011, p. 123). Gum arabic contains 0.22-0.39% nitrogen, 1.5-2.6% protein, 12-16% rhamnose, 15-

16% glucuronic, 24-27% arabinose, 39-42% galactose and about 12.5-16% moisture. Figure 12(b) shows the chemical structure of gum arabic (Azzaoui, et al., 2015). GA quality is evaluated based on factors like odor, color, moisture, viscosity, ash content, PH and concentration of different metals. Minerals found in GA include Na, Ca, P, K, Pb, Cu, Zn, Co, Ni, Cr, Cd and Mn. GA is mostly harvested from arid regions of Chad, Nigeria, Sudan, Ethiopia and Senegal (Patel, 2015).

Production of gum arabic is a natural mechanism of tree to protect itself from mold and insect invasion and uses it to heals its wounds (Cecil, 2005). Gum arabic in Sahara was used as food in the Stone Age (Sanchez, et al., 2018) and bone technologies (bone tools) around 70 000 years ago in south of Africa (E'rrico, 2007) and north east of Africa (Olszewski, et al., 2010).

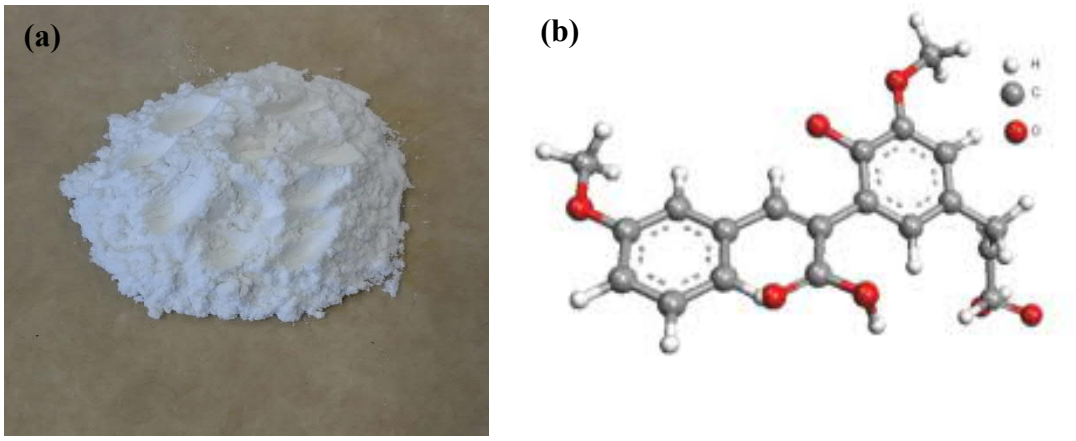


Figure 12. *(a) Gum arabic, (b) Chemical structure of gum arabic* (Azzaoui, et al., 2015)

4000 years ago, Japanese and Chinese used GA for paintings. In addition, Egyptians used gum arabic to prepare inks and watercolors. Gum arabic was also used as adhesive in paints and pigment binders to make hieroglyphs (Scott, et al., 2004).

3.5 Titanium dioxide (TiO_2) as nanoparticles

Titanium dioxide (TiO_2, Titania) is a metal oxide that is widely used in everyday life. It is a white powder (Figure 13) and can have three different phases: anatase, rutile and brookite. TiO_2 is a white solid powder. Anatase form is used for different applications like filters, lithium-ion batteries, anti-reflective or high reflective coatings and has been a target for huge investments. However, it is still a challenge to keep anatase phase stable from transforming into rutile (Theivasanthi & Alagar, 2013). Anatase phase can be converted to rutile phase when heated at high temperatures of more than 600°C (Collazzo, et al., 2011).

Titanium dioxide is chemically inert. However, it shows photocatalytic activity with light that has an energy equal or higher than its band gap energy. TiO_2 is also a semiconductor material. These attributes offer an extensive range of utilizations. Consequently, in view of the moderately low cost of the crude material and its preparation, titanium dioxide has obtained much attention over the last decade (Skocaj, et al., 2011). Titania is considered as a natural material, which at least adds to its positive acceptance by the people. In general, most titanium dioxide are synthesized from minerals like $FeTiO_3$ by using chloride or sulfate. The yearly overall generation of TiO2 powder in 2005 has been estimated to be five million tons (Backus, 2007).

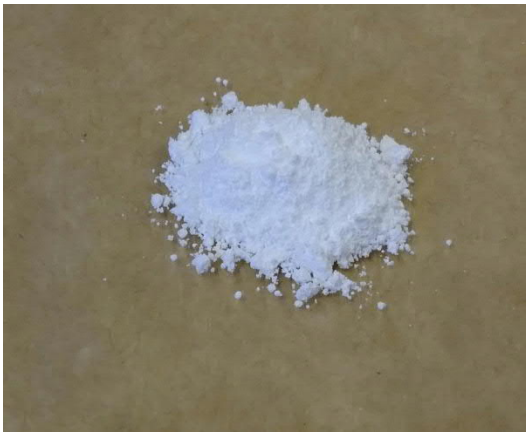


Figure 13. *Titanium dioxide is a white powder.*

Amid late decades, TiO2 powders have started to show up in numerous applications, because of its capacity to present whiteness and opacity on different items, for example, paints, papers and beauty care products. High technological attractiveness starts from its light-dispersing properties and high refractive index, which imply that generally low levels of the pigment are required to have a white coating. Particle size affects the range of wavelength of the light that is scattered. Various innovative enhancements, based on nano-sized titania, have been presented that empower its utilization for self-cleaning coatings and antifogging on glass, for building exteriors, in the plastics business, in confectionary and etc. Moreover, TiO_2 is acknowledged as a nourishment and pharmaceutical added substance (Rowe, et al., 2003).

4. PARAMETERS / SAMPLE FABRICATION

Table 2 briefly shows the binder materials, solutions, percentages, nanoparticles, substrate and the way of coating, which will be explained in the rest of this chapter in detail.

Table 2. *Sample fabrication and parameters*

Binders	Pine tar (Terva) ZeinBaniadam PMMA Gum arabic
Solvents	Acetone for pine tar and PMMA, Ethanol 70% for Zein, Water for gum arabic and Isopropanol for TTIP
Concentrations	5%, 1% and 0.2%
Substrate	Glass micro-slide with dimension of 76mm×26mm×1mm
Binder's coating method	Spin coating (2000 rpm in 10 seconds)
Nanoparticles	TiO_2
Precursor for nanoparticles	TTIP
Concentration (mg/ml)	50
Nanoparticle's deposition method	Liquid Flame Spray (LFS)
Liquid feed rate (ml/min)	5.95
No. of sweeps	5
Line speed (m/min)	50
Distance between burner and a sample (cm)	20
Gas flow rates (l/min) H_2/O_2	50/15

4.1 Binder solutions

PMMA with particle size of 600 microns, manufactured by Good Fellows Company, was dissolved in acetone, purchased from VWR Company. 5%, 1% and 0.2% solutions were

made and all solutions were rested for 24 hours in order to let PMMA dissolve completely in acetone. Same process was repeated to make the solutions from the pine tar, obtained from Motonet shop, using acetone as a solvent. Again, same concentrations were used to make solution out of gum arabic, purchased from Kymin Palokärki Company, with distilled water as a solvent and Zein from Sigma Aldrich Company with ethanol-water solution with 70% ethanol content. Ethanol 99.5% for the solution was purchased from Altia oyj.

4.2 Spin coating of the binder and the oven treatment

Spin coater was used to coat the surface of substrates with binders. Micro-slide glass with dimension of 76mm×26mm×1mm was used as the substrate. All glass slides were cleaned first by acetone then with isopropanol and at the end washed by distilled water. For coating of the substrate with pine tar, Zein, PMMA and gum arabic, spin coater was adjusted to 2000 rpm for 10 seconds. After spin coating stage, all samples were put in the oven for 2 minutes in 300°C in order to increase adhesion especially in the case of PMMA and gum arabic. Therefore, thin films of binders on top of the glass are not washed away in contact with water.

4.3 Deposition of nanoparticles

For depositing titanium dioxide nanoparticles by LFS, titanium (IV) isopropoxide (TTIP, 97% Alfa Aesar) was dissolved in isopropanol to make precursor with titanium concentration of 50 mg/ml. After the preparation of the solution, it was placed in an infusion pump that injects the solution with feed rate of 5.95 ml/min through a tube to the flame. Ratio of hydrogen and oxygen volume flow rates as mentioned in table 2 was tuned for the flame. Distance between flame and sample holder was adjusted to 20 cm. For coating, the substrates with binders, as described above, were attached to the holders. Finally, titanium dioxide nanoparticles were deposited on to the substrates in five sweeps through the flame with 50 m/min line speed. The reaction of TTIP that produces titania occurs according to the following reaction (Coourtecuisse, et al., 1996):

$$TTIP \rightarrow TiO_2 + 4\,C_3H_6 + 2\,H_2O \tag{4}$$

All of reference substrates that have only thin film of binder also were coated for five times with isopropanol with feed rate about 5.54 ml/min in order to have a same treatment as the TiO_2 samples.

4.4 Tests for nanoparticle adhesion

To study the issue of particle detachment from the substrate, sets of measurement with different concentration of binders were carried out. In this stage, six samples were prepared from each binder concentrations and put inside the petri dish that contained 30 ml Methylene blue. Table 3 shows the definition of each sample in detail.

Table 3. *Sample details for photocatalytic test*

1	Clean microscopy glass slide
2	Binders 5%, 1% or 0.2%
3	Binders 5%, 1% or 0.2% plus TiO_2 nanoparticles
4	Binders 5%, 1% or 0.2% plus TiO_2 nanoparticles that has been 15 minutes in ultrasonic bath
5	Binders 5%, 1% or 0.2% plus TiO_2 nanoparticles that was abraded two times (2X)
6	Binders 5%, 1% or 0.2% plus TiO_2 nanoparticles that was abraded 10 times (10X)

For checking the wear resistance, two different wearing techniques were used in this study; abrasion and ultrasonic bath (Table 3). In abrasion a lint free cloth (VWR: 115-2056) with a 317 g weight that produces a 6 kPa pressure was dragged 2 and 10 times over the sample surface (Figure 14(a)). In the case of ultrasonic bath sample were inserted in a distilled water for 15 minutes (Figure 14(b)), after the treatment, sample was dipped in clean distilled water to remove suspension residue.

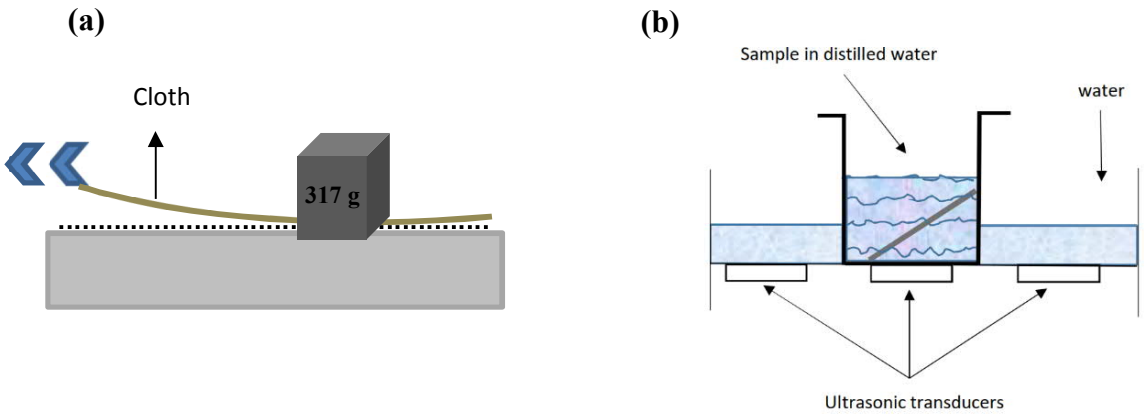


Figure 14. *(a) Abrasion with a weight and a cloth, (b) Ultrasonic bath diagram*

Next step after abrasion and ultrasonic bath was to prepare six samples for photocatalysis test. Six Petri dishes were prepared. Order of samples (microscope glass as substrate) from one to six is, clean micro glass, thin layer of binder (which can be pine tar, Zein, PMMA or GA), binder and titanium dioxide, binder and titanium dioxide after ultrasonic bath, binder and titanium dioxide after two times scrubbing and binder and titanium dioxide after ten times scrubbing respectively.

Methylene blue was diluted in distilled water in order to make a 0.015mMol solution. At the end, 30 ml methylene blue was added to each petri dish with sample inside. Photo was taken from the petri dish that contains clean microscopy glass plus 30 ml methylene blue and one extra petri dish that has clean microscopy glass and 30 ml distilled water in order to have a range of color degradation of methylene blue from blue to transparent. All six samples were put in the UV chamber as shown in Figure 15.

UV chamber contains UVB-lamps (six Sankyo Denki 15 W UVB). UV exposure time between imaging were 0, 10, 20, 40, 70, 100, 130 and 150 minutes. After each exposure time, pictures were taken from all of the six samples in order to figure out the photocatalytic activity of the titanium dioxide by monitoring the color change of methylene blue.

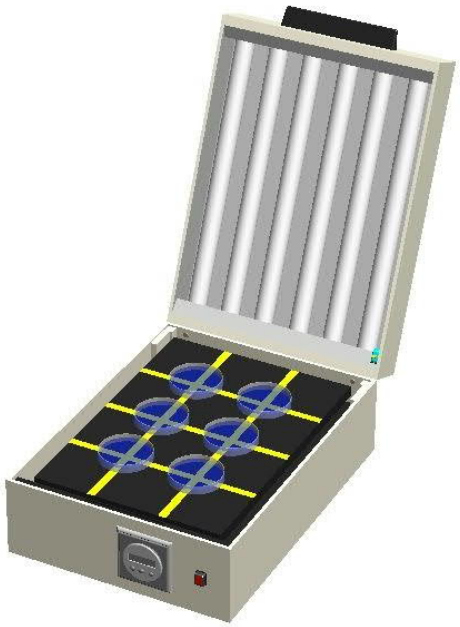


Figure 15. *The used UV chamber and the location of the samples.*

When all photos were taken, Matlab program was used to figure out methylene blue reaction coefficient and the methylene blue concentration according to equations (2) and (3) for each set of samples with different binders.

4.5 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) uses focused beam of electrons to obtain information of the sample surface. The images produced by SEM have high resolution and provide compositional, morphological and topographical information. In order to have better SEM images, samples should be conductive, therefore all of them were coated with carbon.

For this stage, samples with 1% concentration from pine tar, Zein, gum arabic and PMMA plus titania nanoparticles on top of them were prepared for SEM images. Also, SEM images from clean glass and titanium dioxide on glass were prepared in order to have a better understanding of the structure of each of the samples.

5. RESULTS AND DISCUSSION

In this section, results of each binder and comparison with only TiO_2 nanoparticles on glass without binders, will be evaluated separately. Methylene blue concentration as a function of the UV exposure and the activity of TiO_2 will be shown for each of the binders with three different concentrations (5, 1 and 0.2%) in separate graphs. In all graphs the alphabet (U) refers to ultrasonic bath.

5.1 Pine tar

The results of the photocatalysis test on pine tar 0.0, 0.2,1 and 5% with TiO_2 nanoparticles are presented in Figure 16. Parts (a), (c), (e) and (g) show concentrations of MB as a function of the UV exposure and (b), (d), (f) and (h) parts illustrate the slope of the lines presenting the activity of the samples. Strong release of TiO_2 nanoparticles is observed in unscrubbed samples. Ultrasonic bath removed less amount of titanium dioxide compared to the two times (2X) scrubbing, which showed an acceptable level of activity, but in the ten times (10X) scrubbing more particles were removed and less activity was left.

When there is no pine tar film in the samples, ten times (10X) scrubbing has removed all of the titanium dioxide nanoparticles from the glass surface, therefore there is same activity as the reference (Figure 16(b)). When there was pine tar binder in the samples, nanoparticles of titanium dioxide were fixed more on top of substrate even after ten times scrubbing. Among all concentrations, pine tar with 1% concentration shows better results than the others. Part (f) of Figure 16 clearly demonstrates the activity of the TiO_2 in the case of ultrasonic bath and the two times scrubbing of the samples are the same, and even in ten times abrasion still there is a good level of activity.

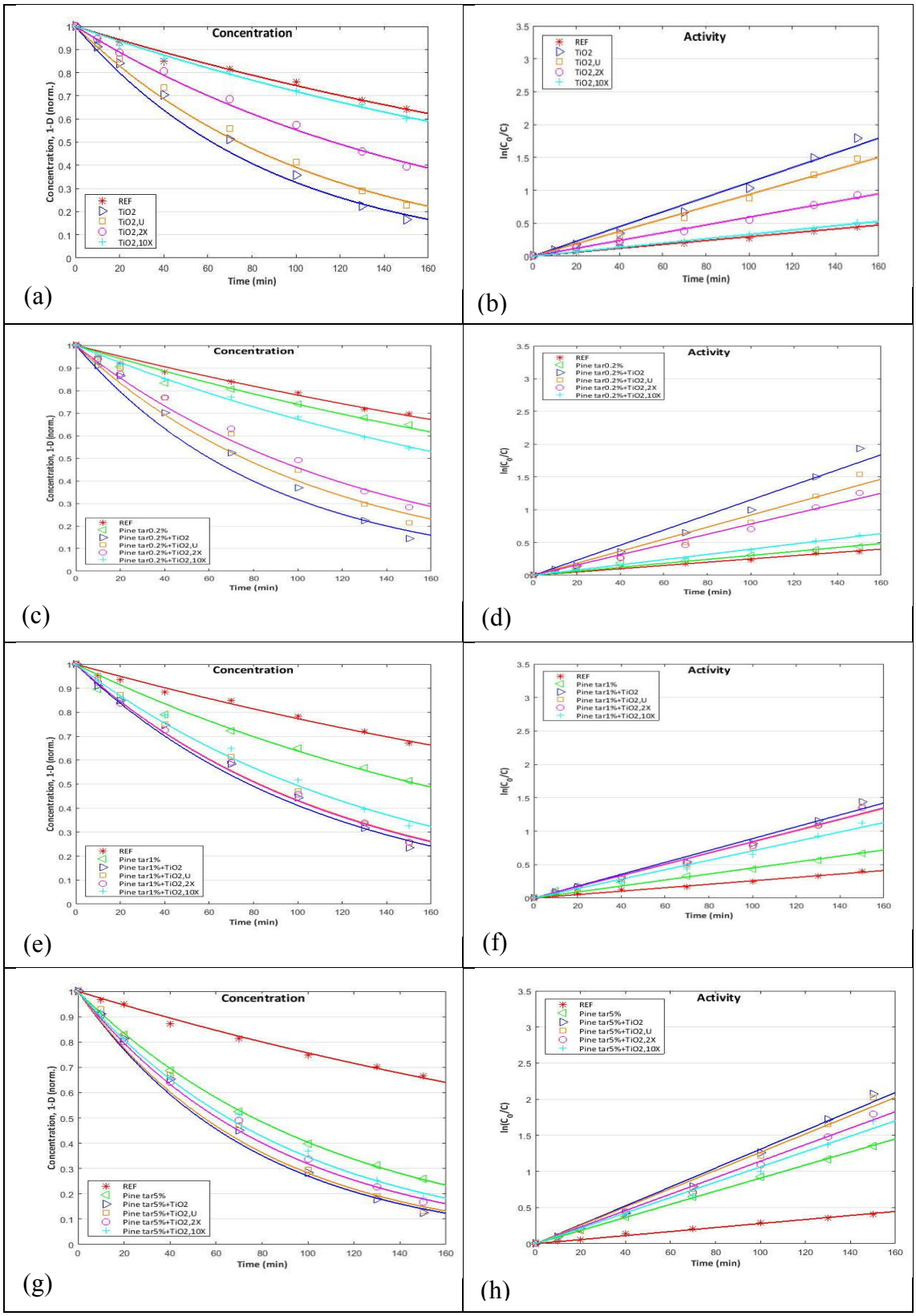


Figure 16. *Concentration of MB as a function of UV exposure and activity of TiO_2 for (a) & (b) 0.0% pine tar and TiO_2, (c) & (d) 0.2% pine tar and TiO_2, (e) & (f) pine tar 1% and TiO_2, (g) &(h) pine tar 5% and TiO_2*

In 5% concentration of pine tar, the problem was that methylene blue was absorbed by thin film of pine tar and Figure 16(g) shows how dramatically concentration of methylene blue dropped just by comparing to the reference (clean glass in 30 ml methylene blue) with pine tar 5% on glass. This fact was observed in other concentrations of pine tar except in the mildest case. Section 5.5 will explain the effect of MB absorption on substrate in detail.

5.2 Zein

The result of the photocatalytic test on Zein with different concentrations plus TiO_2 nanoparticles are shown in Figure 17. Same as before parts (a), (c), (e) and (g) present concentrations of MB as a function of the UV exposure and parts (b), (d), (f) and (h) illustrate the slope of the lines presenting the activity of the samples. Inspecting the graphs of activity shows that the slopes are the same at each concentration. More activity can be seen in unscrubbed samples than in the samples with ultrasonic bath or even two and ten times scrubbed samples. Activity of ten times (10X) scrubbed sample with 0.0% of Zein is close to the reference, which tells that the abrasion removed all of the TiO_2 nanoparticles from the substrate. However, other concentrations of Zein show strong activity of TiO_2 even with ten times scrubbing, which reveals the level of performance of the Zein as a binder for nanoparticles.

Figure 17(h) illustrates Zein with 5% concentration and activity slopes in two and ten times scrubbing are really close to the unscrubbed cases. This trend repeats in the sample of Zein with 1% concentration (Figure 17(f)) and little bit weaker in Zein with 0.2% concentration (Figure 17(d)).

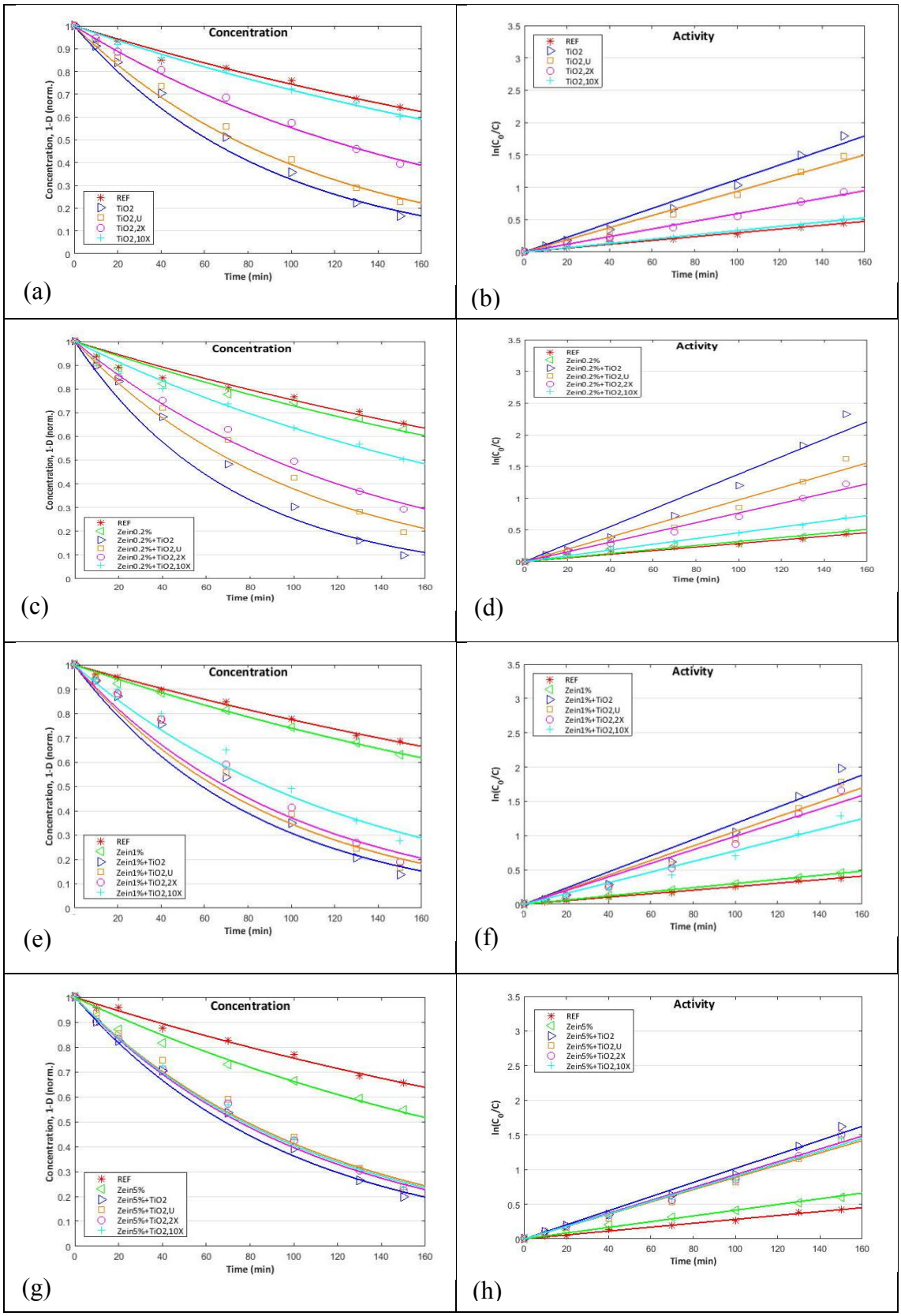


Figure 17. *Concentration of MB as a function of UV exposure and activity of TiO_2 for (a) & (b) 0.0% Zein and TiO_2, (c) & (d) 0.2% Zein and TiO_2, (e) & (f) Zein 1% and TiO_2, (g) &(h) Zein 5% and TiO_2*

Again, like with pine tar binder, Zein binder in higher concentration absorbs methylene blue therefore the concentration of MB for Zein on glass is less than only glass in methylene blue. In order to have a better understanding, measurements were redone on samples with 1% Zein concentration from previous stage to explain methylene blue absorption and the result will be presented in section 5.5.

5.3 Polymethyl Methacrylate (PMMA)

Photocatalysis results for PMMA with concentrations of 0.0, 0.2,1 and 5% plus TiO_2 nanoparticles are presented in Figure 19. Figure 19(a) & (b) shows strong release of TiO_2 nanoparticles in the unscrubbed samples. Ultrasonic bath removed less amount of titanium dioxide compared to two times (2X) scrubbing and an acceptable level of activity is observed. In ten times (10X) scrubbing more particles were removed and less activity was left.

Graph (d) from Figure 19 illustrates, TiO_2 activity slopes for two times scrubbing and ultrasonic bath for the samples with 0.2% concentration of PMMA are the same. However, in 1% concentration, activity of ultrasonic bath sample (Figure 19(f)) is slightly less than with two times scrubbing and in 5% concentration (Figure 19(h)) activity of TiO_2 after ultrasonic bath is even lower and it is the same as with ten times scrubbing.

The only down side about this binder is, PMMA film layer was released easily from the top of the glass substrate after ultrasonic bath or even just in methylene blue with UV exposure (Figure 18).

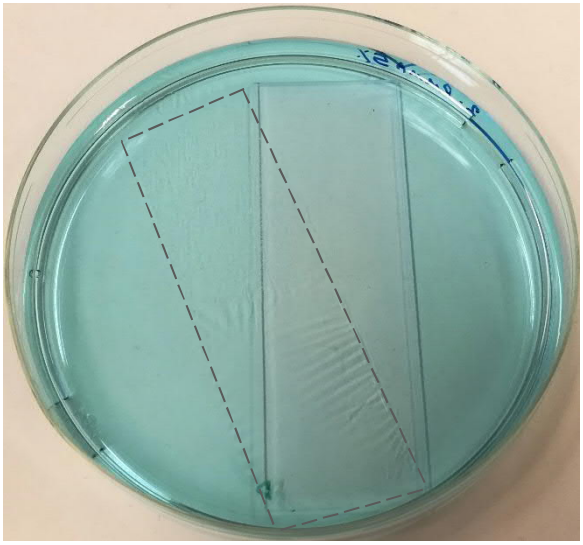


Figure 18. *Removal of PMMA thin film from the glass substrate*

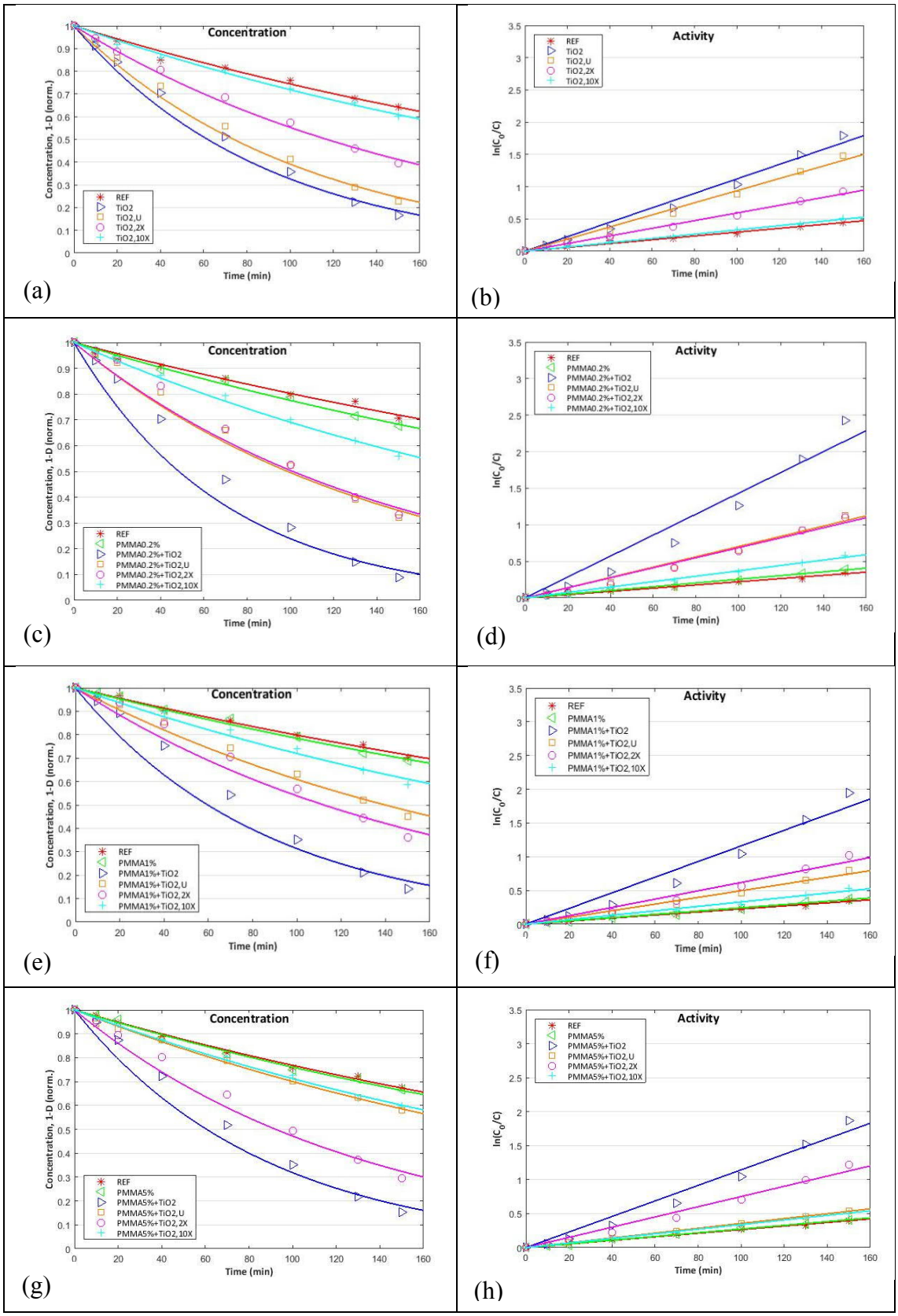


Figure 19. *Concentration of MB as a function of UV exposure and activity of TiO_2 for (a) & (b) 0.0% PMMA and TiO_2, (c) & (d) 0.2% PMMA and TiO_2, (e) & (f) PMMA 1% and TiO_2, (g) &(h) PMMA 5% and TiO_2*

The common factor about PMMA binders in different concentrations is that the ten times scrubbing of the samples removed nearly all of the nanoparticles from the top of the substrate. Good thing about PMMA as a binder is that it does not absorb any methylene blue.

5.4 Gum Arabic (GA)

In this case, the slopes of the activities are different for each concentration of gum arabic. In Figure 20(b) activity on TiO_2 for ten times scrubbed sample is close to reference. Similar results can be seen in GA with 0.2% concentration (Figure 20(d)). In 1% concentration (Figure 20(f)) slight changes are observed; slope of TiO_2 activity for two times scrubbed sample is close to unscrubbed sample. Also, TiO_2 activity in the sample with ten times scrubbing is similar to ultrasonic bath sample.

Results in 5% gum arabic changed dramatically (Figure 20(h)); activity increased significantly, and, additionally, the samples with two times scrubbing and ten times scrubbing show great activity compared to the samples with GA with 0.0% concentration.

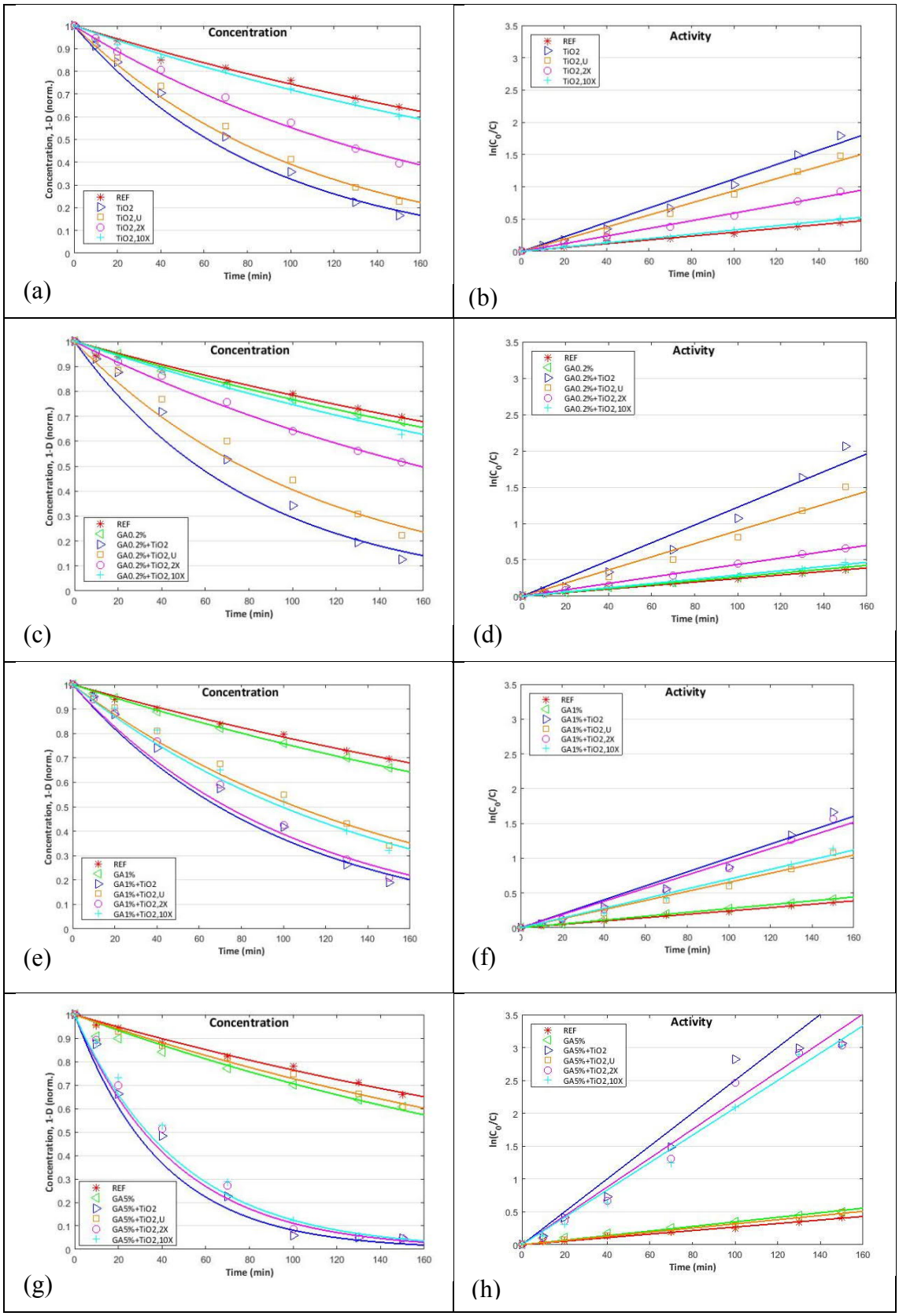


Figure 20. *Concentration of MB as a function of UV exposure and activity of TiO_2 for (a) & (b) 0.0% GA and TiO_2, (c) & (d) 0.2% GA and TiO_2, (e) & (f) GA 1% and TiO_2, (g) &(h) GA 5% and TiO_2*

The only explanation is titanium dioxide nanoparticles penetrate in thick film of gum arabic (5%) during the LFS coating and when the sample is in MB under UV exposure, GA film was dissolved in the methylene blue. Consequently, all TiO_2 nanoparticles were released in MB, which increases the MB degradation because of the large surface area available for reactions.

5.5 Effect of methylene blue absorption on substrate

Among all of the samples with different binders in this research, pine tar and Zain samples absorbed more color when they were in the methylene blue solution. Higher concentrations of the binders in the samples results in thicker coatings, which absorb more color. Some photocatalysis measurement tests were redone on pine tar and Zein with 1% concentration in order to understand for how long the thin films absorb color from the MB solution. Samples with pine tar 1% and Zein 1% with titania nanoparticles from previous measurement were flushed in distilled water and again they were ready for new photocatalytic measurements.

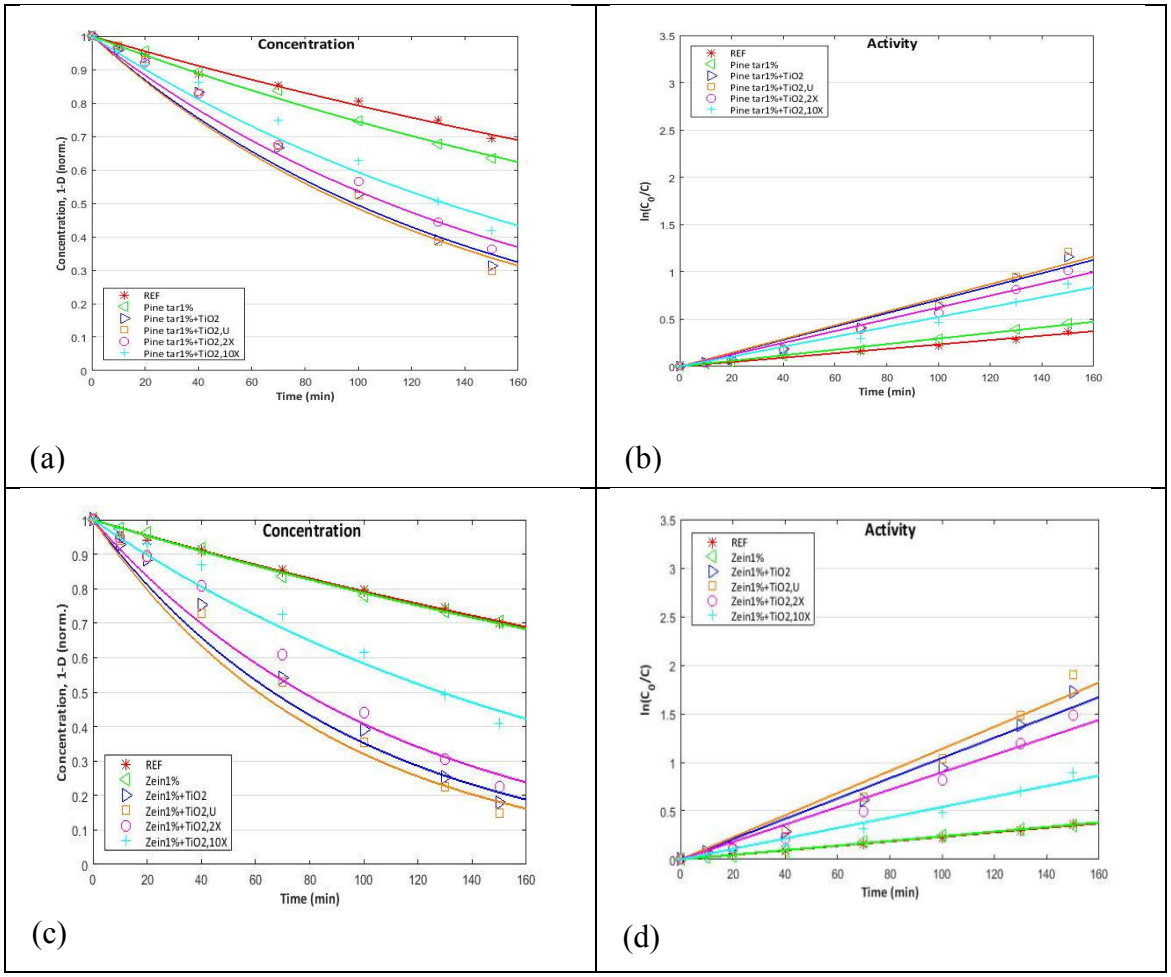


Figure 21. *Concentration of MB as a function of UV exposure and activity of MB for (a) & (b) Flushed 1% pine tar and TiO_2, (c) & (d) Flushed 1% Zein and TiO_2*

Figure 21(b) shows methylene blue in the remeasurement process, where it was observed that less MB was absorbed than in the first time measurement and even in the Zain binder (Figure 21(d)) there was not any absorption, which tells samples are saturated by methylene blue.

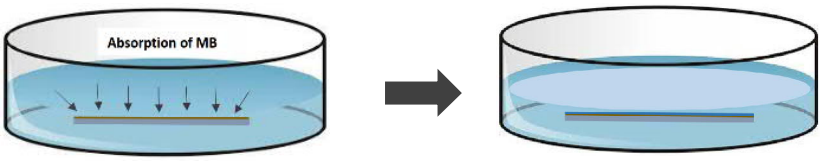


Figure 22. *Methylene blue absorption by pine tar or Zein film on top of a glass substrate*

Pine tar and Zein films absorb methylene blue and the color of sample change to blue, therefore concentration of methylene blue in petri dish is reduced (Figure 22). This absorption affects the photocatalysis test results.

5.6 Comparisons between binders (5% and 0.2%) plus TiO_2

In this section in order to have a better picture, in high concentration (5%), we want to know which binder plays the best role as an adhesive. Therefore, Photocatalytic activity of samples with pine tar, Zein, gum arabic and PMMA with 5% concentration plus titanium nanoparticles on top were compared to the reference (clean glass in methylene blue) and TiO_2 nanoparticles on top of the glass (Figure 23(a) & (b)).

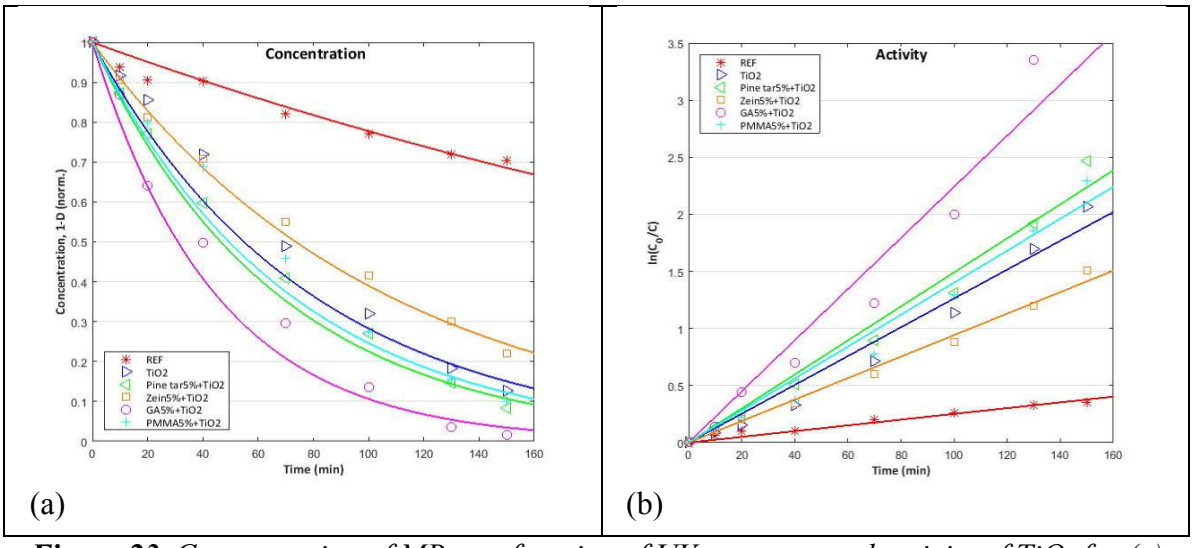


Figure 23. *Concentration of MB as a function of UV exposure and activity of TiO_2 for (a) & (b) pine tar, Zein, GA and PMMA with 5% concentration plus TiO_2 nanoparticles with sample that has TiO_2 nanoparticles without any binders*

Figure 23(b) shows, degradation of the methylene blue as a function of the UV exposure was increased in the cases of gum arabic, pine tar and PMMA compared to TiO_2 sample without any binders. For Zein photocatalytic activity is less than for TiO_2.

In this part, we applied low concentration (0.2%) in order to have a better picture which binders were the best adhesives. Therefore, photocatalytic activity of the samples with pine tar, Zein, gum arabic and PMMA with 0.2% concentration plus titanium nanoparticles on top were compared with reference (clean glass in methylene blue) and TiO2 nanoparticles on top of the glass without any binders (Figure 24(a) & (b)).

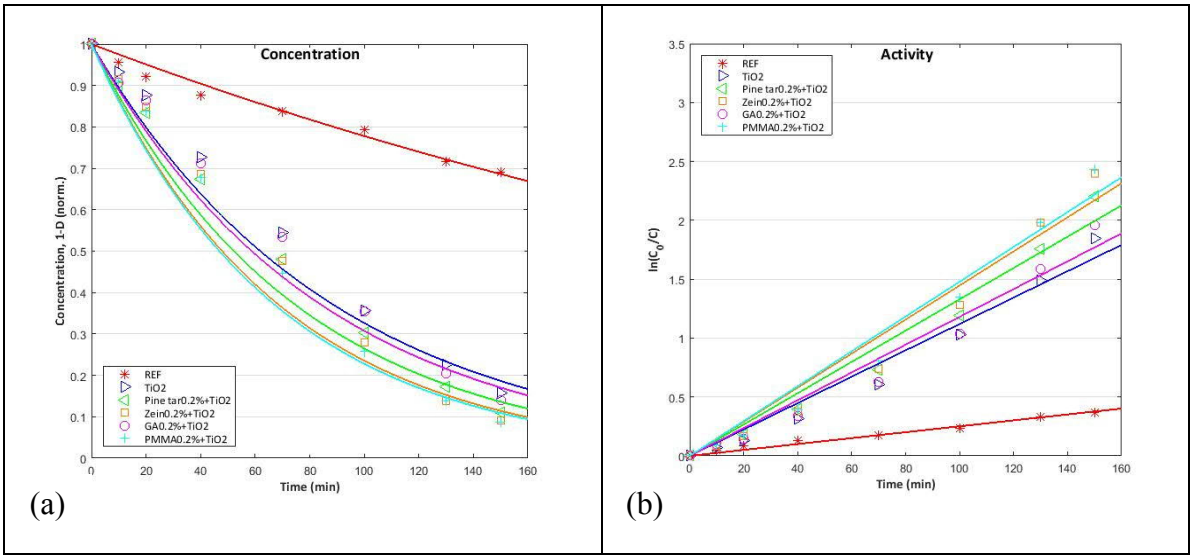


Figure 24. *Concentration of MB as a function of UV exposure and activity of TiO_2 for (a) & (b) pine tar, Zein, Ga and PMMA with 0.2% concentration plus TiO_2 nanoparticles with sample that has TiO_2 nanoparticles without any binders*

Figure 24(b) illustrates Photocatalytic activity of samples with binders (0.2%) and titanium dioxide nanoparticles are higher than sample that only has TiO_2 nanoparticles.

5.7 Summary of photocatalysis test

Four different binders (pine tar, Zein, PMMA and GA) with four concentrations of 0.0, 0.2, 1 and 5% were tested to understand which binders increase the adhesion of the nanoparticles to the substrate. In all graphs, blue color refers to binder with 5% concentration, orange color refers to binder with 1% concentration, gray color refers to binders with 0.2% concentration and yellow color refers to 0.0% binder, which means there is only TiO_2 nanoparticles on top of substrate. Red dashed line refers to reference that came from average reaction coefficients of clean microscopy glasses in 30 ml of methylene blue.

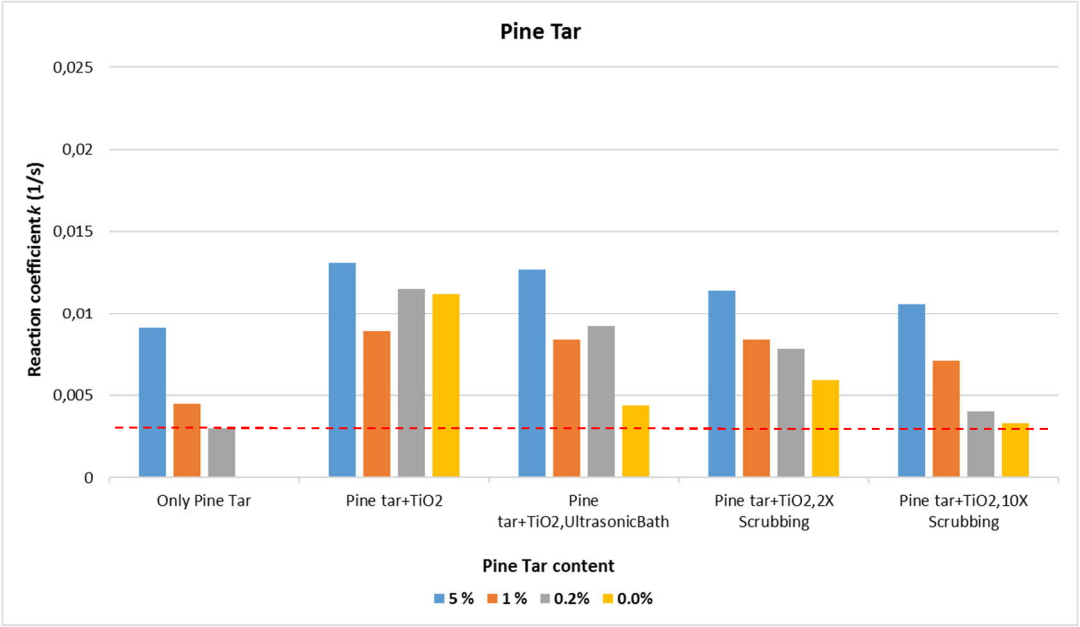


Figure 25. *Reaction coefficient comparison between pine tar with concentration of 5, 1, 0.2 and 0.0% plus TiO_2 nanoparticles on glass substrate*

In figure 25 in pine tar reference (REF) section, reaction coefficient of pine tar with 5% concentration is much higher than the two other concentrations, which means that the color of methylene blue absorbed by pine tar (Figure 22) that affects the result of photo-catalytic activity. Pine tar with 0.2% concentration shows less color absorption compared to 1% concentration. Pine tar with 1% concentrate shows better reaction coefficient in the case of unscrubbed, ultrasonic bath and scrubbing two and ten times compared to the other concentrations and even with titanium dioxide without any binder. Result evaluation shows that the pine tar with 1% concentration is better adhesive because it absorbs less color from methylene blue and does not let nanoparticles release from the substrate.

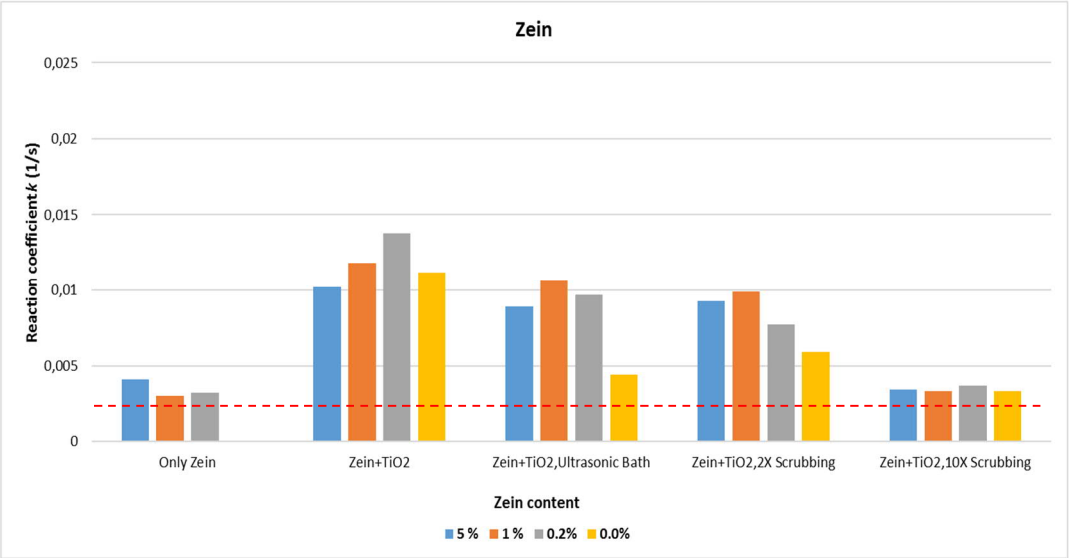


Figure 26. *Reactions coefficient comparison between Zein with concentration of 5, 1, 0.2 and 0.0% plus TiO_2 nanoparticles on glass substrate*

Zein with concentration of 0.2% is better than the other concentrations in unscubbed and ten times scrubbed samples (Figure 26). Zein with 1% concentration is good in ultrasonic bath and two times scrubbed cases. Generally, Zein with 0.2% shows better results among the other concentrations.

Photocatalytic results in the case of PMMA with 0.2% are good in unscrubbed, ultrasonic bath and ten times (10X) scrubbing (Figure 27). However, PMMA with 5% concentration plays a better role as a binder between the substrate and the titanium dioxide nanoparticles in two times (2X) scrubbing.

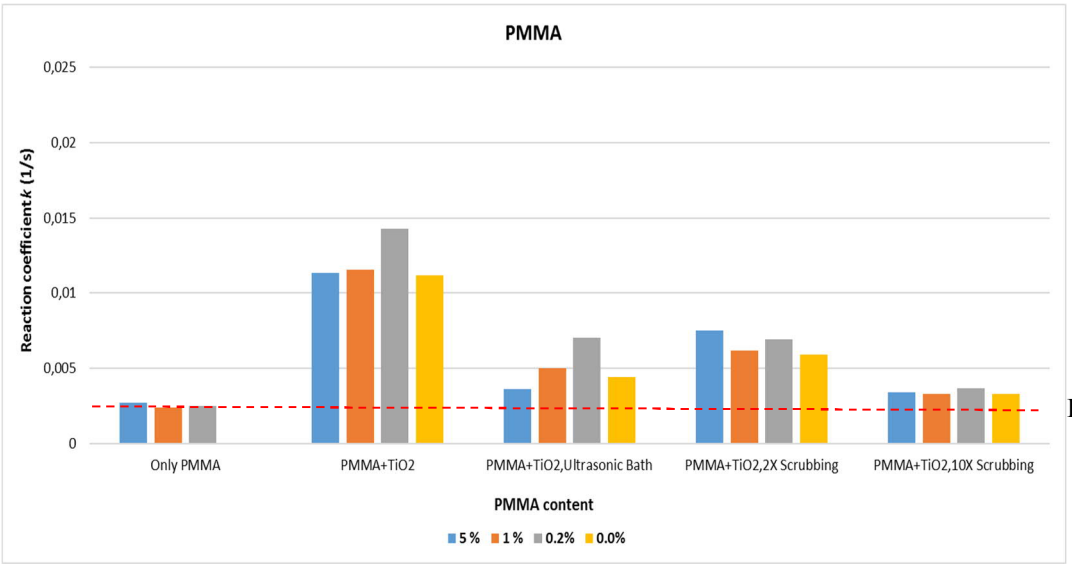


Figure 27. *Reactions coefficient comparison between PMMA with concentration of 5, 1, 0.2 and 0.0% plus TiO_2 nanoparticles on glass substrate*

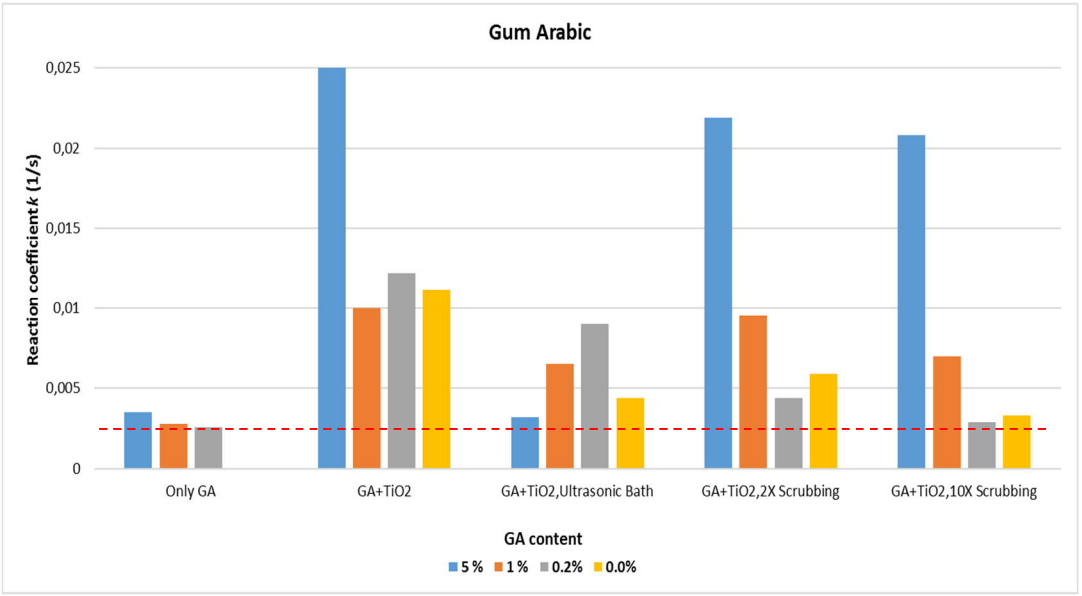


Figure 28. *Reactions coefficient comparison between gum arabic with concentration of 5, 1, 0.2 and 0.0% plus TiO_2 nanoparticles on glass substrate*

In Figure 28, gum arabic with 5% concentration shows a higher result than the other concentrations and the reason was explained back in section 5.4. Gum arabic with 1% concentration shows good adhesive manner in the cases of two and ten times scrubbing. Generally, 0.2% GA shows acceptable results.

Figure 29(a) shows all samples including binders with 0.2 concentration plus titanium dioxide nanoparticles having more reaction coefficient than only titanium dioxide nanoparticles on glass. However, clearly in the 5% concentration case, gum arabic, PMMA and pine tar with TiO_2 nanoparticles on top have more reaction coefficient than only titanium dioxide nanoparticles on glass. In addition, Zein binder with 5% concentration is shown to have lower reaction coefficient than only TiO_2 sample (Figure 29(b)).

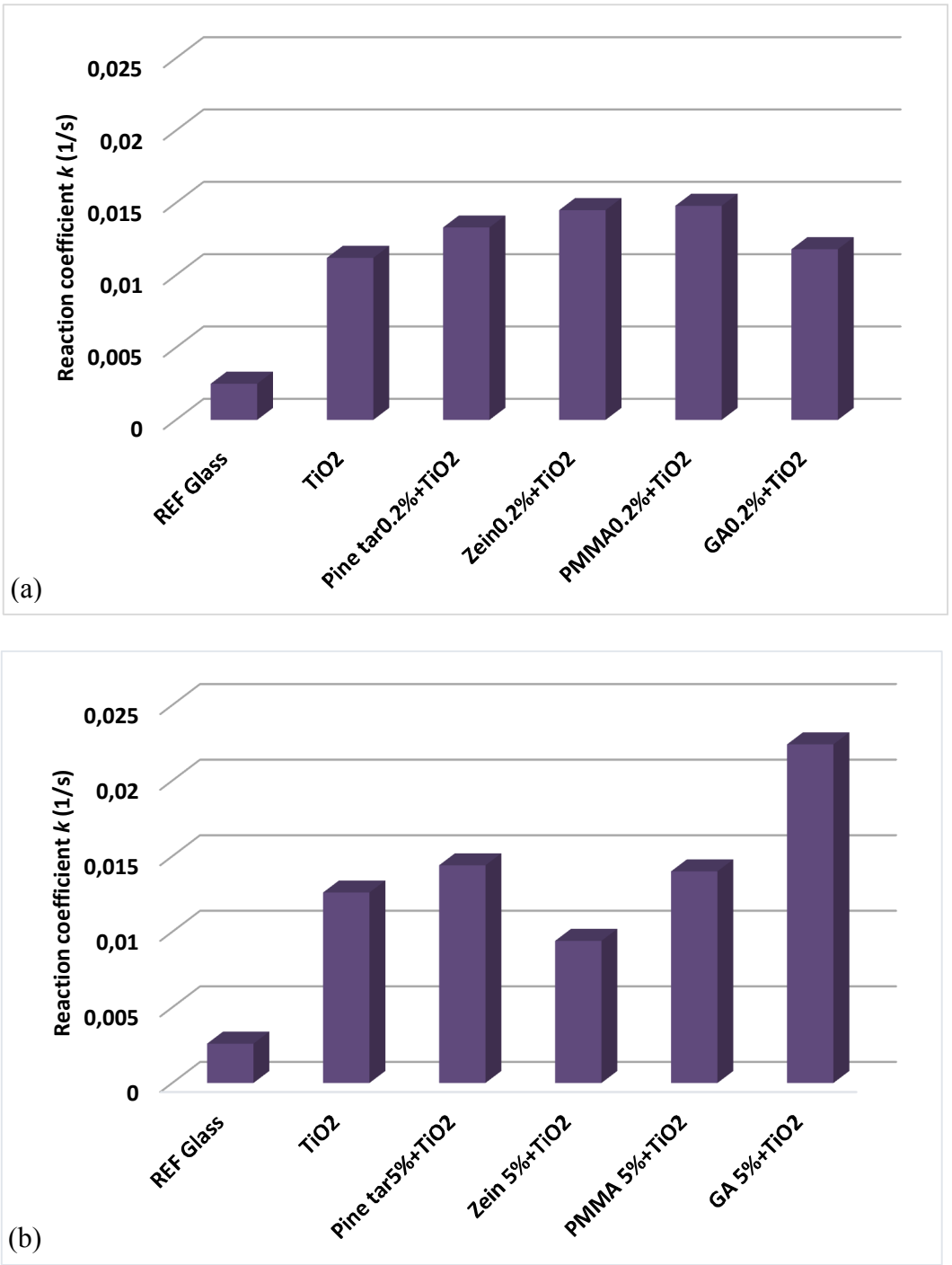


Figure 29. *Reactions coefficient comparison between TiO_2 nanoparticles on glass and Binders plus TiO_2 nanoparticles (a) concentration of 0.2%, (b) concentration of 5%*

All in all, pine tar 0.2 and 5% show similar results. For Zein 0.2%, reaction coefficient is less than Zein with 5% concentration. For PMMA results in both concentrations are the same and for GA 5%, reaction coefficient is two times more than GA 0.2%.

5.8 SEM images

Scanning Electron Microscope images of all four binders were prepared. Concentration of all binders in this section was 1%. SEM images of all four binders before and after TiO_2 nanoparticles deposition was studied in order to have a better understanding of the structure of each of the binders.

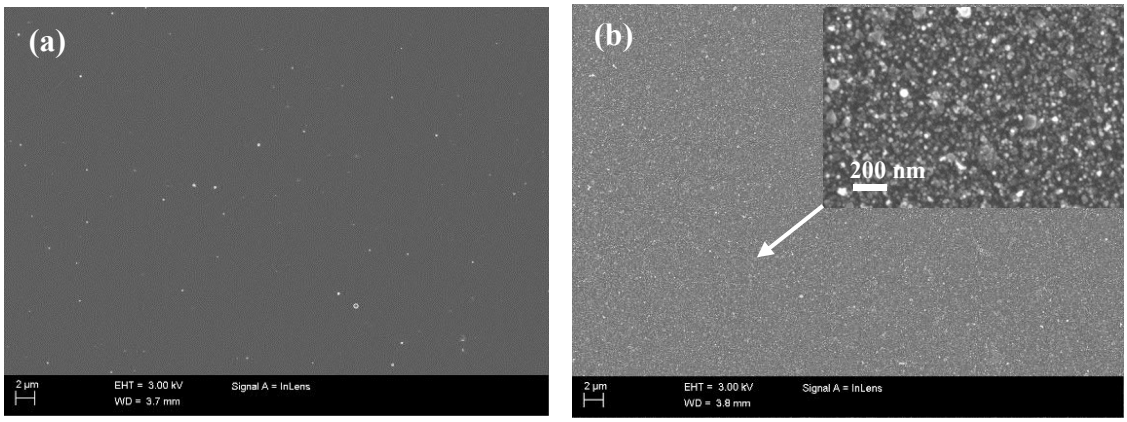


Figure 30. *SEM micrographs of the glass (a) before and after (b) TiO_2 nanoparticles coating*

Figure 30(a) shows SEM micrograph of clean glass that has no nanoparticles on top of it. Image (b) demonstrates titanium dioxide nanoparticles on top of the glass without any binders and where the nanoparticles fully cover the substrate.

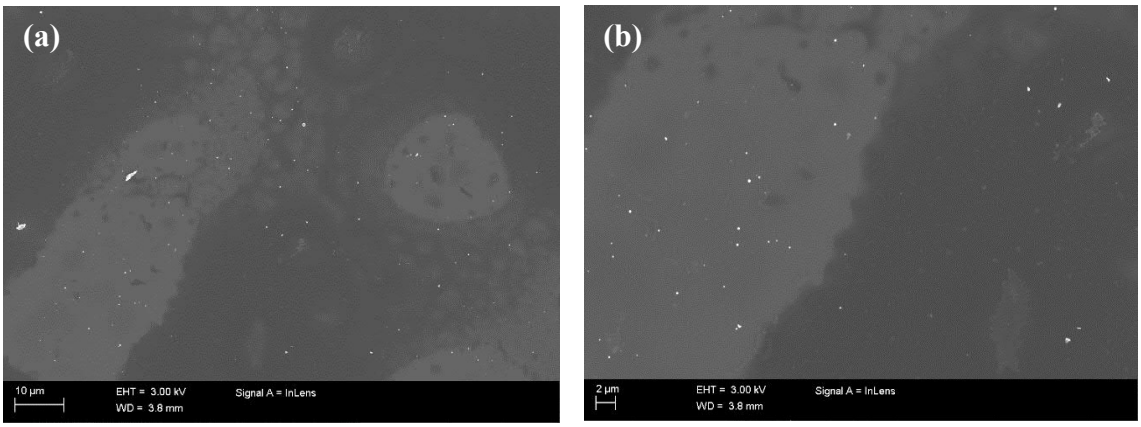


Figure 31. *SEM micrographs of of pine tar's thin film with 1% concentration on top of glass, (a) In low magnification, (b) In high magnification*

Figure 31 shows SEM image of pine tar thin film on top of the glass substrate before nanoparticles deposition. There are some islands that seem have more pine tar in those areas. The surface is not homogeneous in this case. Figure 32 demonstrates, titanium dioxide nanoparticles covered the whole surface of pine tar thin film on top of the glass substrate and even the darker areas that seem to have less pine tar still they have good amount of nanoparticles.

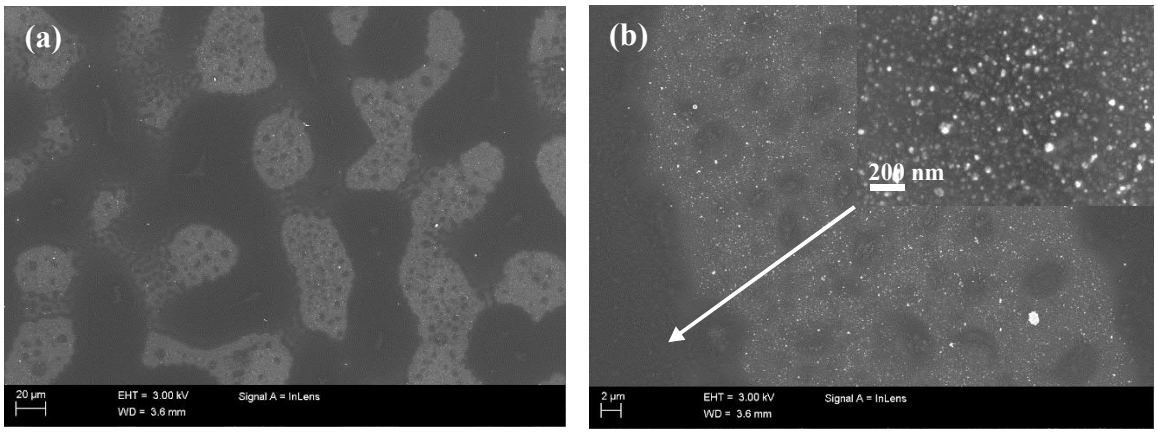


Figure 32. *SEM micrographs of of pine tar's thin film with 1% concentration plus TiO_2 nanopartocles on top of glass, (a) In low magnification, (b) In high magnification*

Figure 33(a) & (b) illustrate two times scrubbing was wiped both titanium dioxide nano particles and pine tar film with 1% concentration from top of the glass and in some areas only surface of the substrate (glass) appeared.

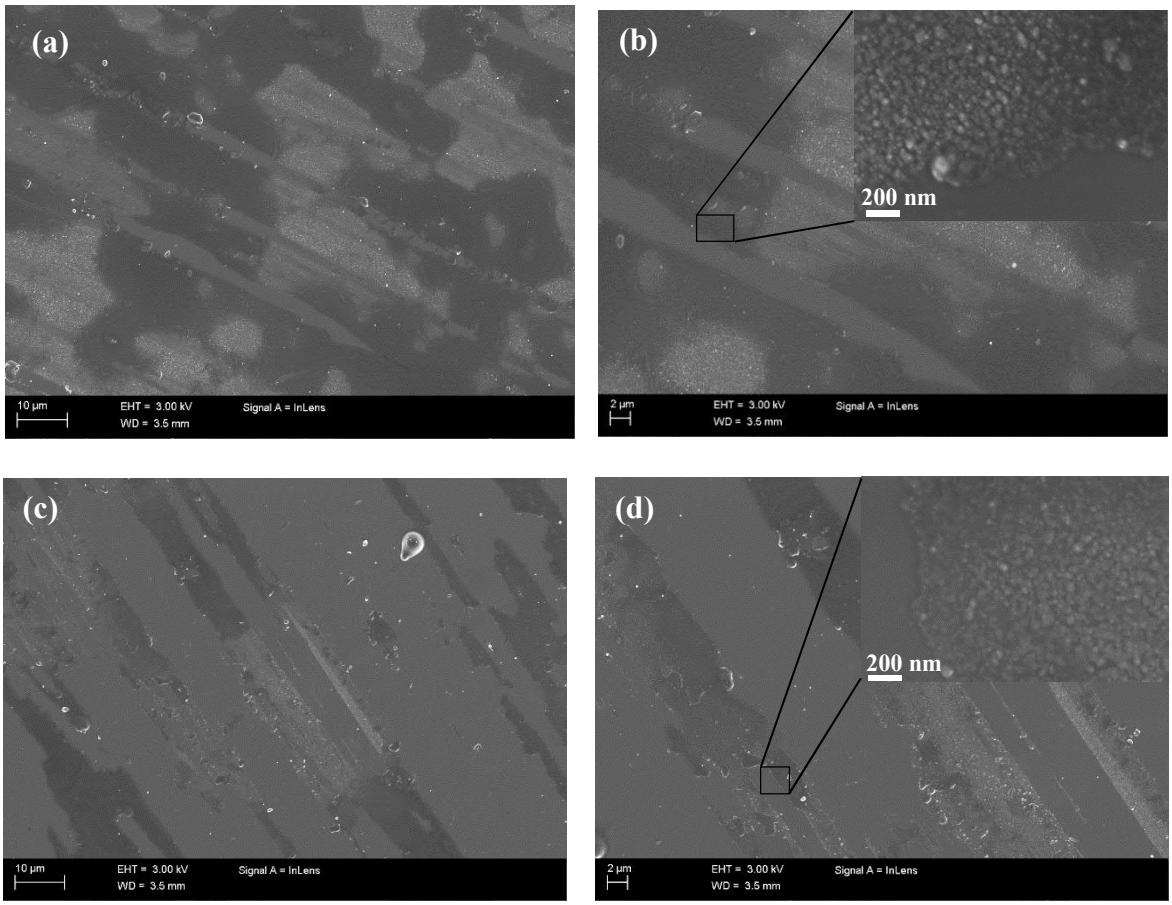


Figure 33. *SEM micrographs of of pine tar thin film with 1% concentration plus TiO_2 nanopartocles on top of glass (a and b) after two times scrubbing, (c and d) after ten times scrubbing*

In ten times scrubbing of pine tar with 1% concentration plus titanium dioxide nanoparticles, more pine tar film and nanoparticles were wiped from surface as it predicted (Figure 33(c) & (d)).

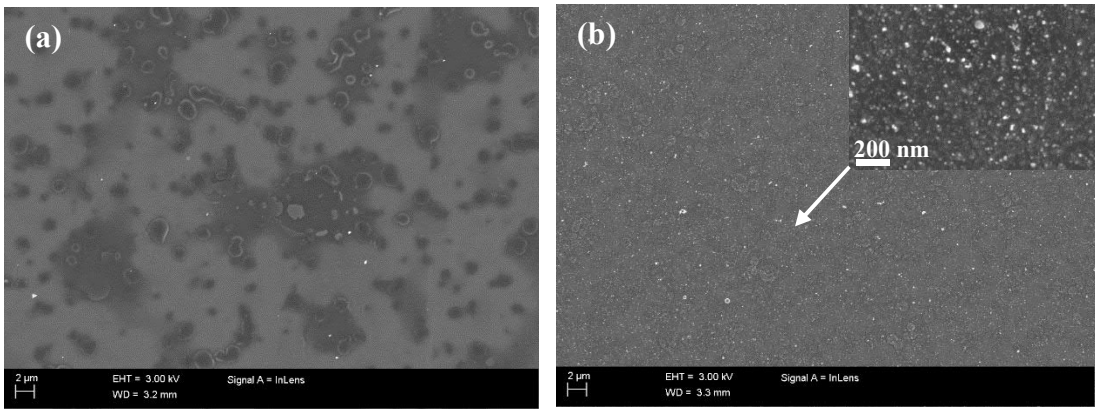


Figure 34. *SEM micrographs of the Zein with 1% concentration (a) before and after (b) TiO_2 nanoparticles coating*

SEM micrograph of Zein with 1% concentration on glass shows many big and small islands (Figure 34(a)) and part (b) shows TiO_2 nanoparticles cover the whole area smoothly and islands from part (a) are barely recognazable.

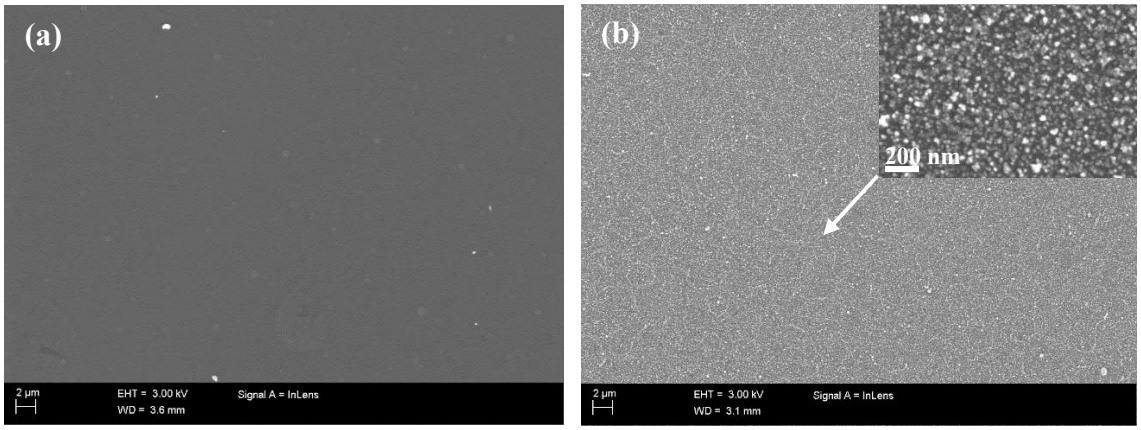


Figure 35. *SEM micrographs of the PMMA with 1% concentration (a) before and after (b) TiO_2 nanoparticles coating*

SEM image of thin film of PMMA with 1% concentration (Figure 35(a)) is really similar to SEM image of a clean glass (Figure 30(a)). After coating, titania nanoparticles cover the whole surface of PMMA film homogeniously (Figure 35(b)).

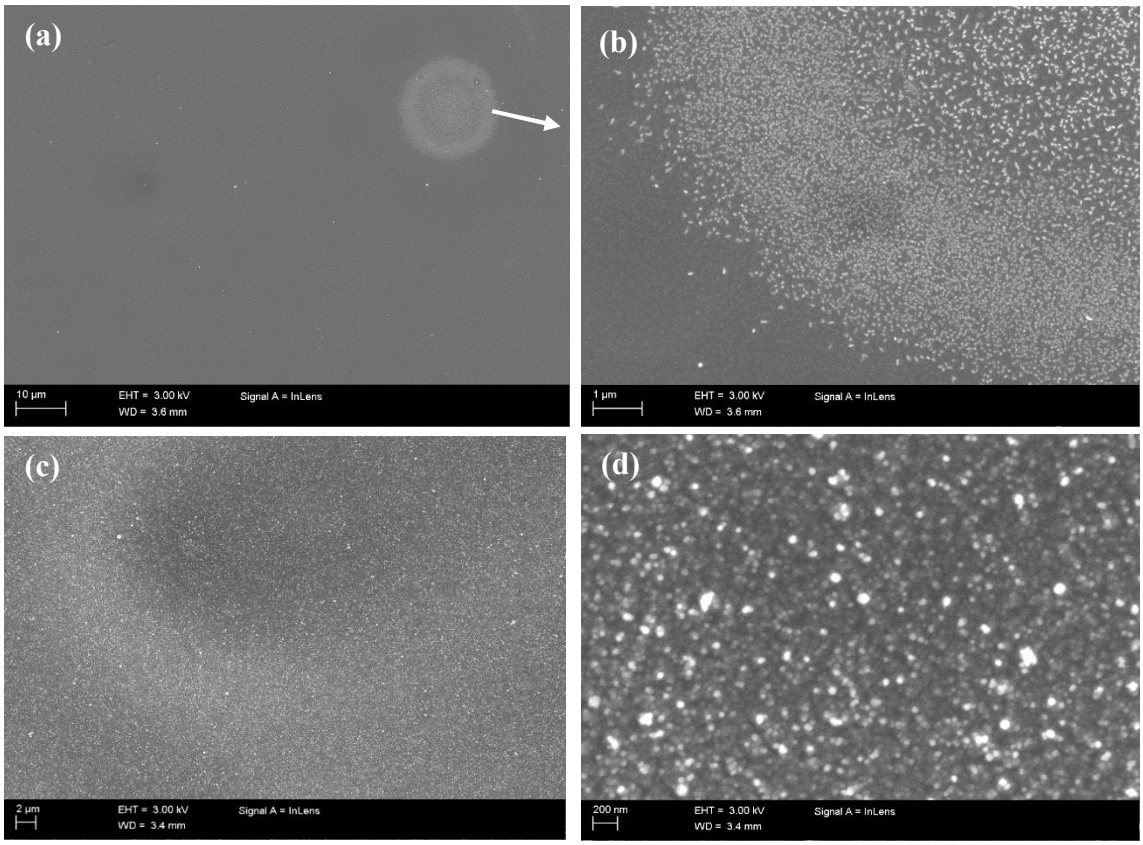


Figure 36. *SEM micrographs of the GA with 1% concentration (a & b) before and after (c & d) TiO_2 nanoparticles coating*

Figure 36(a) shows the SEM micrograph of a thin film of gum arabic with 1% concentration on top of the glass. There is a round area in image that is magnified and consists of small particles which might be undissolved gum arabic in water (Figure 36(b)). part (c) of Figure 36 shows SEM image of gum arabic after titanium dioxide nanoparticles deposition. All surface of the GA film was covered by nanoparticles (Figure 36(d)).

6. CONCLUSION

In this thesis, four binders: pine tar, Zein, gum arabic and PMMA, have been used to make thin films on top of the glass substrates. Titanium dioxide (TiO_2) nanoparticles were synthesized and deposited onto the substrate by Liquid Flame Spray (LFS) method.

Photocatalytic reaction coefficient for TiO_2 in pine tar with 5% concentration is much higher than the two other concentrations, however absorption of methylene blue by pine tar has affected the results of the photocatalytic activity. Pine tar with 0.2% concentration was shown to have less color absorption compared to the 1% concentration. Pine tar with 1% concentrate was shown to have better reaction coefficients in the cases of unscrubbed, ultrasonic bath and scrubbing two and ten times compared to the other concentrations and even with only titanium dioxide on glass without any binder. Result evaluation demonstrated that the pine tar with 1% concentration is a better adhesive because it absorbs less color from the methylene blue solution and does not let nanoparticles release from the substrate. Zein with concentration of 0.2% was better than the other concentrations in the case of unscubbed and ten times scrubbed samples. Zein with 1% concentration was also good in ultrasonic bath and two times scrubbed cases. Generally, Zein with 0.2% was shown to have better results among the other concentrations. Photocatalytic results in the case of PMMA with 0.2% were good in unscrubbed, ultrasonic bath and ten times (10X) scrubbing. However, PMMA with 5% concentration was shown to play a better role as a binder between the substrate and the titanium dioxide nanoparticles in two times (2X) scrubbing. Gum arabic with 5% concentration had higher results than the other concentrations, the reason for this was that the titanium dioxide nanoparticles penetrated in to the thick film of gum arabic (5%) during the LFS coating, and when the sample is in MB under UV exposure, GA film was dissolved in the methylene blue. Consequently, all TiO_2 nanoparticles were released in the MB, which increase activity of TiO_2 because of the large surface area available for reactions. Gum arabic with 1% concentration shows good adhesive behavior in the cases of two and ten times scrubbing. Generally, 0.2% GA was demonstrated to have acceptable results.

SEM images of all the samples, which contain binders with 1% concentration, were studied before and after titanium dioxide nanoparticles deposition. SEM image of pine tar contains many islands. Zein SEM images also illustrate islands but in a smaller scale. PMMA and the clean glass both have similar structures based on the SEM images and gum arabic images show some round spots that might be undissolved GA. Finally, SEM images of all binders after TiO_2 coating show titania nanoparticles covering the whole surface smoothly.

Generally, among all the binders in this research pine tar was shown to have a good potential to fix nanoparticles on top of the substrate especially in low concentrations, after

that Zein is an acceptable binder as well. PMMA and GA are in the third and the fourth place respectively. The problem with PMMA thin films in this research was that they released and removed from the glass substrate when they were placed in the methylene blue. Gum arabic dissolves in water. It is difficult to make it strong in contact with liquids.

Some areas related to this work are not covered in great detail that hopefully will be researched in more detail in the near future. For instance, adding some chemical materials on top of the binders to make them more resistant against abrasion and ultrasonic bath. In addition, to make them more stable on top of a substrate by heating treatment. Other substrates such as metal, paper, plastic or wood could also be used to test behavior of the tested binders on top of them. Pine tar, Zein and gum arabic should be used also in the future as they are useful in the medical field due to their nontoxicity and they are biomaterials that can help to make a safe coating in this area.

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